Danish Ministry of the Environment
Environmental Protection Agency

Survey of products with nanosized pigments

- Focusing on products exempt from the Danish Nanoproduct Register

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Title:
Survey of products with nanosized pigments

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Sources must be acknowledged.

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Foreword

The Danish Nanoproduct Register
The Danish Statutory Order on a register of mixtures and articles that contain nanomaterials as well as the requirement for manufacturers and importers to report to the register (BEK No 644 of 13/06/2014) went into force 18 June 2014. According to the Statutory Order, companies marketing certain products with nanomaterials shall notify the products to the Danish Nanoproduct Register.

The products concerned by the Nanoproduct Register are mixtures and articles that are intended for sale to the general public and which contain nanomaterials:

- where the nanomaterial itself is released under normal, or reasonably foreseeable, use of the mixture or article or
- the nanomaterial itself is not released, but substances in soluble form that are classified as CMRs or environmentally dangerous substances are released from the nanomaterial[1].

A number of products are specifically exempt from reporting to the Nanoproduct Register, including (as relevant for this survey):

- Paint, wood preservative, glue and filler that contains pigment on the nanoscale where the pigment is added solely for the purpose of colouring the mixture.
- Articles of rubber, or rubber parts of articles, that contain the nanomaterials carbon black (EINECS No 215-609-9) or silicon dioxide.
- Articles or their labels on which the nanomaterial is used directly as ink, including newspapers, periodicals, magazines, packaging that is not coloured in the mass or dyed, etc.
- Textiles with nanomaterial used as ink or for dyeing.

Products within the scope of this survey
In order to supplement the information on nanomaterials in consumer products collected by the Nanoproduct Register, the Danish EPA has initiated this survey in order to collect information on the exempt products with pigments in the nanosize.

Objectives of the survey
The objectives of this survey are:

- To provide a discussion of pigments *vis-à-vis* the EU definition of nanomaterials,
- To provide an overview of nanosized pigments placed on the EU market,
- To provide an overview of paint, wood preservative, glue and filler, textiles, and printed articles that contain nanosized pigment and rubber, or rubber parts of articles that contain carbon black.

Timing
The survey has been undertaken by COWI A/S (Denmark) from June 2014 to November 2014.

Advisory group
The project has been followed by an advisory group with representations of various stakeholder organisations:

[1] This would e.g. be release of silver ions from products with nanosilver

- Eurocolour (sector group under CEFIC) and the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD)
  - Heike Liewald, Eurocolour
  - Pierfrancesco Fois, ETAD
  - Uwe Hempelmann, Lanxess Deutschland GmbH
  - Klaus Kund, Clariant Produkte (Deutchland) GmbH
- European Council of the Paint, Printing Ink and Artists's Colourants (CEPE)
  - Thomas Sorensen, Beck & Jørgensen A/S
- European Commission; Joint Research Centre, Hubert Rauscher
- Danish National Research Centre for the Working Environment, Keld Alstrup Jensen
- Technical University of Denmark, Steffen Foss Hansen
- Sun Chemical A/S, Ivan Grønning and Lars Toräng
- Danish Coatings and Adhesives Association, Anette Harbo Dahl
- Danish Ecological Council, Lone Mikkelsen

A workshop was held 18 September 2014 with presentations from the Danish EPA, the working group and the advisory group. Furthermore, a written consultation of the advisory group on the draft report has been undertaken.

Steering group
The work has been steered by a steering group consisting of:
- Mikkel Aaman Sørensen, Danish EPA
- Fleming Ingerslev, Danish EPA
- Katrine Bom, Danish EPA
- Carsten Lassen, COWI A/S
- Frans Christensen, COWI A/S.

Summary

Background and objectives

Under the Agreement "Better Control of Nanomaterials" (Danish: “Bedre styr på nanomaterialer”), the Danish EPA has established a Danish Nanoproduct Register and commissioned a number of projects aiming to investigate and generate new knowledge on the presence of nanomaterials in products on the Danish market and assess the possible associated risks to consumers and the environment. The current project is one of these projects.

The Nanoproduct Register has been established via a statutory order (No 644/2014), requiring importers and producers of certain mixtures and articles containing nanomaterials to notify these products with the register if the products are intended for sale to the general public and if nanomaterials may be released during use. The statutory order exempts certain products, including:

- Paints, wood preservatives, glues and fillers that contain pigment on the nanoscale where the pigment is added solely for the purpose of colouring the mixture.
- Articles of rubber, or rubber parts of articles, that contain the nanomaterials carbon black or silicon dioxide.
- Articles or their labels on which the nanomaterial is used directly as ink, including newspapers, periodicals, magazines, packaging that is not coloured in the mass or dyed, etc.
- Textiles with nanomaterial used as ink or for dyeing.

The current survey aims at identifying and, to the extent possible, quantifying products and pigments which would have had to be notified in the absence of these exemptions. In other words, the survey contributes to the overview of consumer products with nanomaterials on the Danish market. In addition, the project aims at discussing whether and which pigments may be considered nanomaterials according to the definition of "nanomaterial" recommended by the European Commission. This is done based on an initial mapping of pigments on the EU market.

The main focus of the study is on exempt paints, wood preservatives, glues and fillers, as well as on coloured textiles. These are the types of products from which contained nanomaterials are most likely to be released under normal and foreseeable use and therefore the types of products, which most likely would have had to be registered in the absence of the exemptions.

The project, however, also addresses:

- applications of pigments for which a notification will be required (e.g. pigments in mixtures which are not specifically exempt), and
- applications of pigments which are generally exempt (e.g. pigments in solid matrices from which the nanomaterial in itself will not be released)

will be addressed in various chapters.

In relation to this and as a support to companies which might have notification obligations, an appendix is included, which include information on pigments in these product categories collected from the Danish Productregister and the Danish EPA's surveys of consumer products. Further, in relation to carbon black in rubber, one could argue that these applications would have been generally out of scope (the nanomaterials will not be released in itself) even without the specific exemption. Carbon black in rubber is anyway addressed in the report.

Approach and methodology
The current survey is based on available information from databases, chemical encyclopaedia, market surveys, reports from relevant organisations, EUROSTAT statistics on trade, the Danish Product Register and dialogue with companies (pigment producers and Danish importers and formulators), EU and Danish trade organisations (for pigments and downstream users of pigments), as well as other scientific institutions and green organisations. Stakeholders have been approached bilaterally, as well as via a reference group. The reference group has discussed preliminary results in a seminar and had the opportunity to comment on the draft final report.

Pigments *vis-à-vis* the EU nano definition
Various activities are on-going at the EU level regarding clarifying which pigments are to be considered nanomaterials according to the EU nano definition. These activities include an EU 7th Framework Programme research project "Nanodefine" (in which pigments are one of the "cases"); a joint activity between European Research, Technology and Development Performers, metrology institutes, and nanomaterials and instrument manufacturers. Still, no common ground has been established in relation to sampling and analytical methods to be used for determining the particle size distribution of pigments and, consequently, no final conclusions have been reached regarding determination of pigments as nanomaterials - or not. An inherent challenge in these activities is that analytical methods commonly used by industry are usually not able to distinguish constituent/primary particles from agglomerates and aggregates. The EU definition refers to the size of the constituent particles and not to the size of the agglomerates/aggregates.

Pigments can be manufactured in various ways, often involving the steps of milling and aggregation of primary/constituent particles in order to reach the preferred pigment size for the desired optical properties. This preferred/optimal size of pigments for opaque preparations is often several hundred nanometers and therefore apparently above 100 nm (and thereby outside the nano-range).

However, based on discussions with stakeholders, including trade organisations and industry, most pigments are likely candidates to be nanomaterials in any case, as the pigments would often be aggregates of constituent particles (primary particles) where the majority is of a size below 100 nm. The EU definition refers to 50% of the number particle size distribution below 100 nm of the constituent particles.

The particle sizes of a commercial pigment is usually determined by manufacturers in terms of the volumetric size distribution of the actual particles (incl. aggregates and agglomerated), whereas the EU nano definition refers to the number particle size distribution of the constituent particles. Such data might therefore be difficult to interpret in relation to deciding whether a pigment is a nanomaterial. Sometimes, however, even the volumetric size distribution might show a "nanotail" of particles in the nano-size, which seems relatively minor by mass/volume (and thus accounts for a minor part of the volumetric size distribution), but can still be used to judge that the nanotail accounts for more than 50% of the particles by number. In these situations, proceeding to more detailed and expensive analytical methods to determine the distribution of the constituent particles in the agglomerates/aggregates would not be needed.

A specific group of pigments (could be termed "nanopigments" or "ultrafine pigments") has its optimum size in the 1-100 nm nano-range. In the production of these pigments, high shear forces are introduced in order to break the suspended agglomerates and aggregates apart to form smaller particles. These pigments clearly fulfil the nano definition.

Often the individual pigments are manufactured in different grades e.g. ultrafine pigment for transparent applications and coarser pigments for opaque applications. The suspended pigments consist of the same constituent particles, but with different levels of aggregation and agglomeration. Examples of applications of ultrafine pigments are transparent coatings e.g. for coloration of wood, some inks e.g. for inkjet applications, transparent plastic films, inks for digital textile printing, pigment for metallic effects and LCD pigments. The market share of these types of pigments is currently estimated at a few percent of the total market, but no statistical market data are available.

Overall, the ultrafine pigments with preferred particle sizes in the nanorange are nanomaterials, whereas other pigments (often providing opaque properties) can largely be considered as candidates for being nanomaterials based on the size distribution of constituent particles in the pigments, even though the pigments consist of larger aggregates and agglomerates of the smaller constituent particles for many applications. No pigments for particular applications have been identified which clearly fall outside the EU nano definition, even though some marketed pigments likely have a larger median size of the constituent particles.

Finally, it should be noted that the EU nano definition is currently subject to review and may, as a consequence, be adapted. It has been outside the scope of the current project to address the consequences for pigments of possible adaptations suggested by various stakeholders.

Pigments on the EU and global market

Overall, a gross list of 573 pigments that may possibly be on the European market was compiled. Of these, 197 were registered under REACH by September 2014. The list did not include fine particles of pure metals such as aluminium or copper used for pigmentary applications.

Titanium dioxide, carbon black and iron oxides are the dominating inorganic pigments globally and in the EU from a volume perspective. Of the total EU pigment volume, titanium dioxide accounts for about 70%, other inorganic pigments for about 25% and organic pigments for about 5%. The overall European pigment market volume was estimated to be about 2,220,000 tonnes in 2013 and appears to be increasing slightly as compared to previous years.

Data on pigment use by application area in the EU have not been available, but a market survey shows that the global market of inorganic pigments (excluding titanium dioxide but including carbon black) is dominated by uses in construction materials (51% of the total), coatings (26%), plastics (8%) and paper (5%), while other applications account for 10%. For the organic pigments, printing inks are the dominant application area (60%), followed by coatings (18%) and plastics (11%), while other applications account for 11%. The areas exempt from the Danish Nanoproduct Register, such as pigments in coatings, plastics, or inks for printed matter, are therefore among the major applications of pigments.

Registered pigments - In total, 197 pigments from the gross list were registered under REACH. Data on registered volume and registered application areas for each pigment were retrieved from ECHA's data dissemination tool and listed. For some of the pigments, e.g. carbon black, non-pigmentary applications may in fact account for the majority of the registered tonnage, but the public portion of the registrations does not include any indication of consumption by application area. The pigments with the major registered tonnage were inorganic titanium dioxide, carbon black, iron oxides, zinc compounds and lead compounds. Twenty-eight inorganic pigments registered by the Inorganic Pigments Consortium accounted for about 1% of the total registered tonnage (based on average values), whereas 119 pigments registered by the Organic Pigments Consortia accounted for about 2%.

Pigments in exempt consumer products with the potential for releases of nanosized pigments

As the assessment of pigments *vis-à-vis* the EU nano definition reached the conclusion that most pigments might be considered nanomaterials, the survey of consumer products that followed included all pigments in the products.

Data from the Danish Productregister - In order to obtain an overview of pigments in mixtures used in Denmark, data were retrieved from the Danish Productregister. In total 177 substances from the gross list of 573 pigments were registered in the Productregister: 34 inorganic pigments accounting for 98% of the total quantity and 143 organic pigments accounting for 2%. The total registered tonnage in 2013 was 28,460 tonnes. The Danish Productregister includes substances and mixtures used occupationally, but it is deemed that most likely, for the main application areas, the pigments in mixtures used by professionals (non-industrial) are not significantly different from the pigments in mixtures used by consumers. Consequently, the information from the Productregister was used as an indication of the pigments most likely to be present in consumer products.

Paint, lacquers and varnishes - The total consumption of paints and varnishes in Denmark in 2013 was approximately 60,000 tonnes with estimated pigment contents of 6,000-9,000 tonnes. About one third of this tonnage is estimated to be used by consumers, mostly as decorative paints for building applications. In total, 166 different pigments are registered for use in paints and varnishes in the Danish Productregister. Of these, titanium dioxide and iron oxides are the main pigments by volume within all groups of paints. Consumer exposure and releases of pigments to the environment may take place during application of the paints, whereas pigments released from the cured paints are usually bound in small particles of the paint matrix. Both dermal and inhalation exposure may take place by application, whereas oral exposure is considered unlikely. The main route for environmental exposure is via wastewater, in particular for water-based paints. For outdoor applications, a fraction of the paint may be released by spill or via aerosols. The emission factors for water-based products are likely higher than the factors for solvent-based.

Adhesives, sealants, putty and filling materials - The total consumption of adhesives, sealants, putty and filling materials in Denmark in 2013 was approximately 20,000 tonnes, with an estimated pigment content of less than 500 tonnes. No data on the quantities used by consumers are available, but these likely represent less than half of the consumption. The number of different pigments used in the products is relatively small and titanium dioxide, iron oxides and carbon black account for nearly 100% of the total quantity. Consumer exposure and environmental exposure routes are almost the same as for paints. The emission factors for water-based products are likely higher than the factors for those that are solvent-based.

Inks on printed matter - The majority of printed matter in Denmark are used by consumers and are thus within the scope of the Nanoproduct Register. Actual measurements of pigments in printed matter for consumers are not available, but pigments in inks used in Denmark for production of printed matter is used as an indicator of the pigments that are present in the printed matter. In total, 108 pigments are registered for this application area in the Productregister. Compared to the other application areas, the organic pigments account for a larger fraction of the pigment in inks, although titanium dioxide and carbon black are still the main pigments by volume. In the printed matter, the pigments are embedded in the polymer matrix of the inks and investigations have shown that no migration of nanosized pigments from the products could be detected. Possible releases of free pigments to the environment from the printed matter during use are considered unlikely. Possible releases of pigments by waste treatment are beyond the limits of this survey.

Textiles - Pigments are used both for dyeing and in printing inks for textiles. Nearly 100% of textiles sold in Denmark are imported and data from the Productregister on pigments in mixtures for textile production in Denmark cannot be considered to provide a representative view of the pigments in textiles sold to consumers. A list of the pigments commonly used in textiles has been adopted from a previous survey of textiles sold in Denmark. Pigments are either applied to textiles with a polymer binder or the pigments are dissolved into the polymer matrix of some coloured synthetic fibres. In both cases, the pigments in the final products are (as described for the final, cured paints) bound into a matrix and will normally only be released as part of small particles of this matrix. Pigments may be released from textiles during domestic washing, but sufficient data on whether the pigments are released as “free pigments” or bound within the binder or the fibre particles during consumer washing activities could not be identified.

Rubber parts that contain carbon black – Based on the available information, it has not been possible to estimate the quantities of carbon black used in rubber in Denmark. However, the tonnage is significant considering that about 90% of the carbon black manufactured globally (capacity is eight to ten million tonnes per year) is used for tyres (70%) and other rubber applications (20%). Pigmentary applications accounting for 9% are largely covered by the application areas addressed above. Carbon black provides a range of properties to the rubber including colouration, but is mainly added to rubber for its reinforcement properties. This is also the case for its main application in tyres, which by abrasion lose 10-20% by weight during their life cycle. Available evidence suggests that carbon black is lost from tyres as part of non-respirable rubber particles and that it will not easily migrate out of this matrix.

Dansk sammenfatning

Baggrund og formål
I henhold til finanslovsaftalen "Bedre Styr på nanomaterialer" for 2012-2015 har Miljøstyrelsen etableret et dansk nanoproduktregister og igangsat en række udredningsprojekter med det formål at kortlægge og generere ny viden om tilstedeværelsen af nanomaterialer i produkter på det danske marked samt vurdere eventuelle risici for forbrugerne og miljøet forbundet med denne anvendelse af nanomaterialer. Nærværende projekt er et af disse udredningsprojekter.

Nanoproduktregisteret er etableret via en bekendtgørelse (nr. 644/2014), som forpligter importører og producenter af visse blandinger og artikler, der indeholder nanomaterialer, at indberette disse produkter til registret, hvis de er beregnet til salg til private, og hvis nanomaterialet kan frigives under brug.

Bekendtgørelsen undtager visse produkter, herunder:
- Maling, træbeskyttelse, lim og udfyldningsmidler, der indeholder pigment i nanostørrelse, hvor pigmentet er tilsat alene med henblik på at farve blandingen.
- Varer af gummi eller gummidele af varer, der indeholder nanomaterialerne carbon black eller siliciumdioxid.
- Varer, hvor nanomaterialet er anvendt som trykfarve direkte på varen eller på mærkater på varen, herunder aviser, blade, magasiner, emballage som ikke er gennemfarvet og lignende.
- Tekstiler, hvor nanomaterialet er anvendt som trykfarve eller til gennemfarvning af tekstiler.

Nærværende undersøgelse har til formål at identificere og, i det omfang det er muligt, at kvantificere produkter og pigmenter, som ville have været indberetningspligtige i fravær af disse undtagelser. Med andre ord bidrager undersøgelsen til at danne et overblik over forbrugerprodukter med nanomaterialer på det danske marked. Desuden har projektet til formål at afklare, hvilke pigmenter som kan betragtes som nanomaterialer i henhold til Europakommissionens anbefalede definition af "nanomateriale" (omtales som EU's nanodefinition). Grundlaget for nærværende undersøgelse er en indledende "top-down" kortlægning af pigmenter på EU-markedet.

Hovedfokus i undersøgelsen er på malinger, træbeskyttelse, lime og udfyldningsmidler, samt på farvede tekstiler i det omfang, de er undtaget fra indberetning. Det er de typer af produkter, for hvilke det er mest sandsynlig, at de indeholdte nanomaterialer kan blive frigivet under normal og forudsigelig brug. Det er derfor de typer af produkter, som sandsynligvis skulle have været indberettet i fravær af ovennævnte undtagelser.

Projektet berører imidlertid også:
- anvendelse af pigmenter i produkter, som vil være indberetningspligtige (f.eks. pigmenter i blandinger, som ikke specifikt er undtaget), og
- anvendelse af pigmenter, der generelt er fritaget (f.eks. pigmenter i faste matricer, hvorfra det frie nanomateriale ikke vil blive frigivet)

Derfor og som støtte til virksomheder, som kan have indberetningspligt, er der inkluderet et bilag, som angiver den viden om pigmenter i disse produkter, som har kunnet hentes fra Produktregistret og Miljøstyrelsens kortlægninger af forbrugerprodukter. Endvidere kunne man argumentere for, at carbon black i gummi ville have været undtaget fra indberetning (nanomaterialerne vil ikke i sig selv blive frigivet), selv uden den specifikke undtagelse. Carbon black i gummi bliver dog alligevel bekrevet i rapporten.

Tilgang og metode
Nærværende undersøgelse er baseret på tilgængelige oplysninger fra databaser, kemiske encyklopædier, markedsundersøgelser, rapporter fra relevante organisationer, EUROSTATs handelsstatistikker, det danske Produktregister (ikke at forveksle med nanoproduktregistret), samt dialog med virksomheder (producenter af pigmenter og danske importører og blandere af kemiske produkter), danske og europæiske brancheorganisationer (for pigmenter og "downstream"-brugere af pigmenter), videninstitutioner og grønne organisationer. Interessenterne er blevet kontaktet bilateralt, samt via en referencegruppe. Referencegruppen har drøftet foreløbige resultater på et seminar og haft mulighed for at kommentere på udkastet til den endelige rapport.

Pigmenter *vis-á-vis* EU's nanodefinition
Der er en række aktiviteter i gang på EU-plan, med henblik på at afklare, hvilke pigmenter som kan betragtes som nanomaterialer i henhold til EU definitionen. Disse aktiviteter omfatter et forskningsprojekt under EU's syvende rammeprogram "Nanodefine", hvor pigmenter er en af de behandlede "cases". Projektet har deltagere fra europæiske forskningsinstitutioner, teknologiudviklere, metrologiske institutter, samt producenter af nanomaterialer og måleinstrumenter. Indtil videre er der dog ikke etableret fælles fodslag i forhold til, hvilke prøvetagnings- og analysemetoder som skal anvendes til bestemmelse af partikelstørrelsesfordelingen af pigmenter. Derfor er der endnu ingen endelige konklusioner vedrørende bestemmelse af, hvorvidt de enkelte pigmenter er nanomaterialer eller ej. En iboende udfordring i forhold til disse aktiviteter er, at de analysemetoder, som almindeligvis anvendes af industrien, normalt ikke er i stand til at skelne primærpartikler (nogle steder omtalt som "ubundne" partikler) fra agglomerater og aggregater. EU definitionen refererer til størrelsen af primærpartiklerne og ikke til størrelsen af agglomeraterne/aggregaterne.

Pigmenter kan fremstilles på forskellige måder, som ofte involverer trinnene formaling og aggregering af primærpartikler for at opnå den foretrukne partikelstørrelse for de ønskede optiske egenskaber. Den foretrukne/optimale størrelse af pigmenter til ikke gennemsigtige anvendelser er ofte flere hundrede nanometer, og derfor tilsyneladende over 100 nm (og dermed uden for nano-området).

Baseret på drøftelser med de berørte interessenter, herunder brancheforeninger og en række pigmentproducenter, vil de fleste pigmenter sandsynligvis kandidere til at være nanomaterialer under alle omstændigheder, da pigmenterne ofte ville være aggregater af primærpartikler hvor hovedparten af partiklerne er under 100 nm. EU definitionen refererer til, at 50% af primærpartiklerne i den antalsmæssige partikelstørrelsesfordeling skal være under 100 nm.

Pigmentproducenterne bestemmer normalt partikelstørrelserne af et kommercielt pigment som den volumetriske størrelsesfordeling af de faktiske partikler (inkl. aggregater og agglomerater), hvorimod EU nanodefinitionen refererer til antallet af primærartikler i partikelstørrelsesfordelingen. Sådanne data kan derfor være vanskelige at fortolke i forhold til at afgøre, om et pigment er et nanomateriale. Indimellem viser selv den volumetriske størrelsesfordeling dog en hale af partikler i nanostørrelse ("nanotail"). Denne hale kan udgøre en mindre procentdel af massen/volumen af partikler (og dermed en mindre procentdel af den volumetriske størrelsesfordeling), men kan i nogle tilfælde bruges til at vurdere, om mere end 50% af antallet af partikler er i nanostørrelse. Hvis dette er tilfældet, vil det i disse situationer ikke være nødvendigt at gå videre til mere detaljerede og kostbare analysemetoder til bestemmelse af fordelingen af de primære partikler i agglomeraterne/aggregaterne.

En specifik gruppe af pigmenter, som ofte betegnes "nanopigmenter" eller "ultrafine pigmenter", har en optimal størrelse i intervallet 1-100 nm. Ved fremstilling af disse pigmenter anvendes kraftig mekanisk påvirkning for at adskille de suspenderede agglomerater og aggregater i mindre partikler. Disse ultrafine pigmenter falder klart under EU nanodefinition.

Det enkelte pigment fremstilles ofte i forskellige kvaliteter, f.eks. som ultrafint pigment til transparente anvendelser og grovere pigmenter til ikke-transparente anvendelser. De suspenderede pigmenter består af de samme primærpartikler, men med forskellige niveauer af aggregering og agglomerering. Eksempler på anvendelser af ultrafine pigmenter er transparente overfladebehandlingsmidler f.eks. til farvning af træ, nogle trykfarver f.eks. til inkjet printere, gennemsigtige plastfilm, blæk til digitalt tekstiltryk, pigmenter som giver metalliske effekter og LCD pigmenter. Markedsandelen for disse typer af pigmenter anslås i øjeblikket at udgøre nogle få procent af det samlede marked for pigmenter, men der er ingen statistiske markedsdata tilgængelige.

Sammenfattende kan ultrafine pigmenter med foretrukne partikelstørrelser i nano-området (1-100 nm) anses for at være nanomaterialer, mens øvrige pigmenter (ofte til ikke-transparente anvendelser), kandiderer til at være nanomaterialer baseret på størrelsesfordelingen af de ubundne/primære partikler i pigmenterne – også selvom pigmenterne til mange anvendelser består af større aggregater og agglomerater af de mindre primærpartikler. Projektet har ikke identificeret anvendelse af pigmenter, som klart og entydigt falder uden for EU nanodefinitionen, selv om nogle markedsførte pigmenter sandsynligvis ikke er nanomaterialer.

Slutteligt skal det bemærkes, at EU nanodefinitionen i øjeblikket er under revision og som følge heraf kan blive tilpasset. Det har været uden for rammerne af nærværende projekt at undersøge, hvorvidt ændringer foreslået af forskellige interessenter kunne influere på, om pigmenter defineres som nanomaterialer eller ikke.

Markedsførte pigmenter - EU og globalt
Samlet set er der opstillet en bruttoliste på 573 pigmenter, som muligvis findes på det europæiske marked. Heraf er 197 blevet registreret under REACH til og med september 2014. Listen omfatter ikke fine partikler af rene metaller, såsom aluminium eller kobber, anvendt som pigmenter.

Volumenmæssigt er titaniumdioxid, carbon black og jernoxider de dominerende uorganiske pigmenter i EU og globalt. Af den samlede forbrug af pigmenter i EU, tegner titaniumdioxid sig for omkring 70%, andre uorganiske pigmenter for omkring 25% og organiske pigmenter for ca. 5%. Det samlede markedsvolumen for pigmenter i Europa er anslået at være omkring 2.220.000 tons i 2013 og synes at være svagt stigende i forhold til tidligere år.

Data og information om pigmenternes fordeling på anvendelsesområder i EU har ikke været tilgængelig, men en markedsundersøgelse viser, at det globale marked for uorganiske pigmenter (ekskl. titaniumdioxid men inklusiv carbon black), er domineret af anvendelser i byggematerialer (51% af det samlede volumen), overfladebehandling (26%), plast (8%) og papir (5%), mens andre anvendelser udgør 10%. For organiske pigmenter er trykfarver det dominerende anvendelsesområde (60%) efterfulgt af overfladebehandling (18%) og plast (11%), mens andre anvendelser tegner sig for 11%. De anvendelser, som er undtaget fra indberetning til det danske nanoproduktregister, såsom pigmenter i overfladebehandlingsmidler, plast og trykfarver i tryksager, er således blandt de største anvendelser af pigmenter.

Registrerede pigmenter - I alt 197 af pigmenterne på bruttolisten er registreret under REACH. Data vedr. de registrerede mængder og anvendelsesområder for hvert pigment er hentet fra kemikalieagenturets (ECHAs) hjemmeside med registreringsdata. For nogle af de registrerede pigmenter, f.eks. carbon black, kan ikke-pigmentanvendelser udgøre størstedelen af den registrerede tonnage, men den offentligt tilgængelige del af registreringerne indeholder ikke angivelse af forbruget opdelt på anvendelsesområder. De største registrerede mængder udgøres af de uorganiske pigmenter titaniumdioxid, carbon black, jernoxider, zinkforbindelser og blyforbindelser. Otteogtyve uorganiske pigmenter registreret af REACH konsortiet for uorganiske pigmenter tegnede sig for omkring 1% af den samlede tonnage (baseret på gennemsnitlige værdier), mens 119 pigmenter registreret af konsortiet for organiske pigmenter tegnede sig for omkring 2%.

Pigmenter i danske forbrugerprodukter med potentiale for udslip af pigmenter i nanostørrelse undtaget fra indberetning
Da vurderingen af pigmenter *vis-á-vis* EU's nanodefinition kom til den konklusion, at de fleste pigmenter kunne anses for at være nanomaterialer, har den videre undersøgelse af forbrugerprodukter omfattet alle pigmenter i produkterne.

Data fra Produktregistret - For at få et overblik over pigmenter i blandinger der anvendes i Danmark, blev der udtrukket data fra det danske Produktregister. I alt er 177 stoffer fra bruttolisten på 573 pigmenter registreret i Produktregistret; 34 uorganiske pigmenter tegner sig for 98% af den samlede mængde og 143 organiske pigmenter tegner sig for 2%. Den samlede tonnage i 2013 var 28.460 tons. Produktregistret indeholder stoffer og blandinger, der anvendes erhvervsmæssigt, men for de vigtigste anvendelsesområder skønnes det sandsynligt, at pigmenter i blandinger, der anvendes professionelt (ikke-industrielt), ikke er væsentligt forskelligt fra pigmenter i blandinger, der anvendes af forbrugere. Derfor blev oplysningerne fra Produktregisteret anvendt som en indikation af, hvilke pigmenter som mest sandsynligt er til stede i forbrugerprodukter.

Maling, lak og fernis - Det samlede forbrug af maling og lak i Danmark var i 2013 ca. 60.000 tons med et anslået indhold på 6.000-9.000 tons pigment. Omkring en tredjedel af dette skønnes at blive anvendt af forbrugere, hovedsagelig som bygningsmaling. I alt 166 forskellige pigmenter er registreret til anvendelse i maling og lak i Produktregistret. Af disse er titaniumdioxid og jernoxider de volumenmæssigt vigtigste pigmenter for alle grupper af malinger. Forbrugereksponering og udslip af pigmenter til miljøet kan ske under anvendelse af malingen, hvorimod pigmenter frigivet fra de hærdede malinger normalt er bundet i små partikler af malingens matrix. Såvel hudkontakt som indånding kan finde sted ved anvendelse, hvorimod oral eksponering anses for usandsynligt. De vigtigste udledninger til miljøet er via spildevand, især for vandbaseret maling. Til udendørs anvendelser kan en del af malingen frigives ved spild eller via aerosoler. Emissionsfaktorerne for vandbaserede produkter er sandsynligvis højere end for produkter baseret på organiske opløsningsmidler.

Lime, fugemasser, kit og fyldmaterialer - Det samlede forbrug af lime, fugemasser, kit og fyldmaterialer i Danmark var i 2013 ca. 20.000 tons med en anslået pigmentindhold på mindre end 500 tons. Der er ingen tilgængelige data om mængden af forbrugeranvendelser, men det er sandsynligvis mindre end halvdelen af forbruget. Antallet af pigmenter, der anvendes i produkterne, er forholdsvist lille, og titaniumdioxid, jernoxider og carbon black tegner sig for næsten 100% af den samlede mængde. Forbrugereksponering og emission til miljøet sker stort set ad de samme veje som for maling. Emissionsfaktorerne for vandbaserede produkter er sandsynligvis højere end for produkter baseret på organiske opløsningsmidler.

Trykfarver på tryksager - Hovedparten af tryksager i Danmark anvendes af forbrugerne, og er således indenfor rammerne af nanoproduktregistret. Faktiske målinger af pigmenter i tryksager til forbrugerne er ikke tilgængelige, men pigmenter i trykfarver, der i Danmark anvendes til produktion af tryksager, kan anvendes som indikator for de pigmenter, som er til stede i de færdige tryksager. Der er i alt 108 pigmenter, som er registreret for denne anvendelse i Produktregisteret. Sammenlignet med de andre anvendelsesområder udgør de organiske pigmenter en større andel af pigmenter i trykfarver, selvom titaniumdioxid og carbon black stadig er de volumenmæssigt vigtigste pigmenter. I tryksager, er pigmenterne indlejret i en trykfarvens polymermatrix, og en undersøgelser har vist, at der ikke kan påvises migration af pigmenter i nanostørrelse fra produkterne. Mulig frigivelse af frie pigmenter til miljøet fra tryksager i brug anses således for usandsynligt. Mulig frigivelse ved affaldsbehandlingen er uden for rammerne af denne undersøgelse.

Tekstiler - Pigmenter anvendes både til indfarvning af tekstiler og i trykfarver til tekstiltryk. Næsten 100% af de tekstiler, som sælges i Danmark, importeres, og data fra Produktregistret om pigmenter i blandinger til tekstilproduktion i Danmark kan ikke anses for at give et repræsentativt billede af pigmenter i tekstiler solgt til forbrugerne. En liste over de pigmenter, der almindeligvis anvendes i tekstiler, er hentet fra en tidligere undersøgelse af tekstiler solgt i Danmark. Pigmenter påføres tekstiler med et polymer-bindemiddel eller pigmenterne er opløst i den polymere matrix i nogle indfarvede syntetiske fibre. I begge tilfælde er pigmenterne i de endelige produkter (som beskrevet for færdighærdede malinger) bundet i en matrix, og vil normalt kun blive frigivet som en del af små partikler af denne matrix. Pigmenter kan frigives fra tekstiler i forbindelse med vask i husholdningerne, men der er ikke fundet indgående viden om, hvorvidt pigmenterne frigives som "frie pigmenter" eller som bundet i bindemidlet.

Gummi/gummidele, som indeholder carbon black - Baseret på de foreliggende oplysninger, har det ikke været muligt at estimere mængderne af carbon black anvendt i gummi i Danmark. Tonnagen er dog betydelig i betragtning af, at omkring 90% af den carbon black som fremstilles globalt (kapaciteten er 8-10 mio. tons om året), anvendes til dæk (70%) og andre gummiprodukter (20%). Pigmentanvendelser, som tegner sig for 9%, er i vid udstrækning omfattet af ovennævnte anvendelser. Carbon black bibringer en række egenskaber til gummi, herunder farvning, men er primært anvendt i gummi pga. sine forstærkende egenskaber. Dette er også tilfældet i hovedanvendelsen i dæk, som ved slid mister omkring 10-20 % af vægten i løbet af deres livscyklus. Foreliggende data tyder på, at carbon black frigives fra dæk som ikke-respirable gummipartikler, og at stoffet kun vanskeligt kan migrere ud af denne matrix.

1. Methodology and scope

1.1.1 Pigments within the scope of the survey

As mentioned in the Preface, the required reporting to the Danish Nanoproduct Register does not include certain mixtures where the pigment is added solely for the purpose of colouring the mixture or where the pigments are used in inks or for dyeing of textiles. Furthermore, articles where the nanomaterial is used in a solid matrix and where the normal use of the article does not result in releases of free nanomaterials, are generally out of scope. This would e.g. apply to most applications of pigments in plastics and other polymers. This survey mainly addresses exemptions where pigments in the nanosize can be assumed to be released.

In this survey (and presumably in the Statutory Order as well) "colouring effect" is used broadly for the interaction between the pigment and visible light which also include other effects such as regular nonselective reflection of light (metallic effect) and opacity.

In the following, the differences between pigments, fillers and dyes are briefly described.

Pigments

Pigments are organic or inorganic, coloured, white or black, fluorescent or metallic materials which are practically insoluble in the medium in which they are dispersed. They are distinct particles that give the medium its colour and opacity.

Pigments maintain their crystalline particle structure throughout the entire dispersion process, and they are practically unaffected physically or chemically by the binder, i.e. the medium into which they are dispersed.

Pigments and dyes are categorized according to their generic name and chemical constitution in the Colour Index (C.I.), published by The Society of Dyers and Colourists, England, and The American Association of Textile Chemists and Colorists (SDC, 2014).

Fillers

Most fillers are very fine particulate solids which may be in the nanosize. Although fillers may provide some colours (or colour modifications) to e.g. a paint or plastic, this is not the main purpose of using the filler. Substances marketed as fillers are considered to be beyond the scope of this survey as products with nanosized fillers are not exempt from the Danish Nanoproduct Register.

Dyes

Like pigments, dyes may be manufactured as fine powders with a particle size distribution which renders the dyes to fall within the definition of nanomaterials. Dyes are, however, soluble colourants; i.e. they are dissolved in the medium and are not present as particles in the final (consumer) products. Soluble dyes are therefore outside the scope of the Danish Nanoproduct Register and therefore also beyond the scope of the current project.

UV-absorption and colouring

Pigments with particles in the nanosize may provide transparency and at the same time absorb UV-light. Whereas the well-known nanosized TiO_2 used in sunscreens and other applications does not have a colouring effect, other nanosized pigments such as iron oxides may have a combined effect of transparency, UV-absorption and colouring (Shangyu, 2014). As the exemptions from the Danish Nanoproduct Register concerns only products where the pigment is added solely for the purpose of colouring the mixture, nanosized pigments added with an intention to provide UV-protection and/or self-cleaning effect (e.g. if marketed as such) are in principle beyond the scope of this survey as these products would have to registered. However, as the authors of this report are not always in a position to assess whether these properties are intended, it is not always possible to exclude products with these properties from this survey.

1.1.2 Objectives

The main objective of the study is to survey consumer products with pigments in the nanosize on the Danish market and assess to what extent nanoparticles may be released from the products. The focus is on pigment application for products exempt from the Danish Nanoproduct Register, i.e.:

- Paint, wood preservative, glue and filler that contains pigment on the nanoscale where the pigment is added solely for the purpose of colouring the mixture.
- Articles of rubber, or rubber parts of articles, that contain the nanomaterials carbon black (EINECS No 215-609-9) or silicon dioxide.
- Articles or their labels on which the nanomaterial is used directly as ink, including newspapers, periodicals, magazines, and packaging that is not coloured in the material itself or dyed, etc.
- Textiles with nanomaterial used as ink or for dyeing.

As information on pigments and particle sizes of pigment in products on the Danish market is not readily available, the first step in the study is a survey of pigments marketed in the EU. The information obtained is then applied to an assessment of where nanosized pigments are most likely marketed in Denmark in relevant consumer products.

However, given the top-down approach applied in this project, it should be noted that:

- applications of pigments for which a notification will be required (e.g. pigments in mixtures which are not specifically exempt), and
- applications of pigments which are generally exempt (e.g. pigments in solid matrices from which the nanomaterial in itself will not be released)

will, predictably, be addressed in various chapters.

In relation to this and as a support to companies which might have notification obligations, a range of appendices are included outlining which pigments are frequently found in various relevant product categories. Furthermore, in relation to Carbon Back in rubber, one could argue that these applications would have been generally out of the scope of the project (nanomaterial will not be released in itself) even without the specific exemption. Carbon black in rubber, in any case, is addressed in this report.

1.1.3 Survey of pigments marketed in the EU

Contact to industry

Contact has been established with the following Danish and International trade organisations:

- Eurocolour – which organise the major players in the European colorants industry. Eurocolour is part of the European Federation of Chemical Producers Associations, Cefic. Eurocolour represents manufacturers of pigments, dyes and fillers, producers as well as manufacturers of food colorants, and ceramic decorating materials.
- ETAD - The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers
- CEPE - European Council of the Paint, Printing Ink and Artists' Colorants
- Euratex - European Apparel and Textile Confederation
- Plastindustrien - The Danish Plastic Federation

- DFL - The Danish Paint and Adhesives Industry (covers also sealants)

As part of the data collection and the discussion of pigments *vis-à-vis* the EU nano definition, a workshop was held with key organisations on 18 September 2014.

Contact to the scientific society and other organisations
Contact has been established with the European Commission Joint Research Centre (JRC), in order to exchange results and views on pigments *vis-à-vis* the European Commission's recommended definition of nanomaterials.

Gross list of manufactured substances
A gross list of pigments has been compiled by combining information from the following sources:
- Pigments registered or planned to be registered by 2018 by the IP consortium (55 substances);
- Pigments registered or planned to be registered by the Organic Pigments consortia (122 substances, of these 43 were registered in the first round);
- Pigments registered by the consortia for titanium dioxide, carbon black, iron oxides and zinc substances (10 substances);
- Registered substances with 'pigment' in the name or synonym name (125 substances – many of these are included in the lists mentioned above);
- CPMA Classification of Chemical Descriptions and Usage of the Complex Inorganic Color Pigments. CPMA (2013). (58 pigments of which 57 are preregistered, 1 substance was registered and not included in the lists mentioned above);
- List of commercially available organic pigments (Herbst *et al.*, 2005). (313 substances of which 299 are pre-registered);
- Pre-registered substances with 'pigment' in the name or synonym name (241 substances of which many are included in the lists above);
- Inorganic pigments listed in Kirk Othmer Encyclopedia (2005).

In total, the gross list consists of 573 substances.

The list does not include metal pigment, which consists of fine particles of e.g. copper or aluminium, as these pigments cannot be distinguished from other applications of the metal in retrieval of data from REACH registrations or the Danish Productregister.

Pigments registered under REACH
The pigments registered under REACH are listed in Appendix 2.

Inorganic pigments - Inorganic pigments registered or planned to be registered by 2018 by the IP Consortium, representing 26 leading manufacturers and importers of inorganic pigments, was retrieved from the consortium's website (IP Consortium, 2014). The website furthermore provided some overall information on the applications of each of the pigments.

Organic pigments – For the registration of organic pigments, seven consortia were formed by 12 leading manufacturers and importers of organic pigments and for the first phase of the REACH registrations (2010), whereas five consortia have been formed for the second phase of registrations (by 2013). Lists of organic pigments registered in the first and second rounds have been obtained from ETAD.

Other consortia - Pigments registered by the consortia for titanium dioxide, carbon black, iron oxides and zinc substances were retrieved from the websites of the consortia. For some of these substances (e.g. zinc oxide) the application as pigment is only one of several applications.

Search on "pigment" - Furthermore, a search on ECHA's registration database using "pigment" in the search category "name" gave 125 results, of which 36 substances were not indicated by the consortia mentioned above. These were cross-checked with the pigments included in the list of commercially available substances in the book "Industrial organic pigments"; the pigment class and C.I. index colour name was retrieved from the list (Herbst *et al.*, 2005).

ECHA registration database - For the registered pigments, information on tonnage and additional information on end-uses were retrieved from ECHA's dissemination database of registered substances (ECHA, 2014).

Properties of pigments

Properties of the individual pigments have been obtained from:

- ECHA's registration database. The published portion of the registrations includes information on "Particle size distribution" under physical and chemical properties.
- Technical data sheets from manufacturers.

Properties have been obtained for selected pigments. It was initially expected that data of particle size distribution for all pigments would be obtained, but on the basis of the discussion of pigments *vis-à-vis* the EU definition of nanoparticles, it was later decided that this information would be obtained for selected pigments only.

1.1.4 Survey of consumer products with nanosized pigments in Denmark

Inventory of pigments registered in the Danish Productregister

The gross list of 573 substances was used for data retrieval from the Danish Productregister. It turned out that some of the pigments from the list of commercially available organic pigments (Herbst *et al.*, 2005) had no longer used CAS numbers. In total, the revised list for the data retrieval consisted of 568 substances. Data on pigments in produced, imported, and exported mixtures were extracted by pigment, application area, and sector of economic activity. The data were processed in order to remove confidential information. The data are further described in section 4.1.

Trade statistics

Data on production, import and export of relevant consumer products were extracted from Eurostat from the statistics on industrial production and international trade (prom) combining production, import and export by the PRODCOM (production statistics) nomenclature. The PRODCOM classification is based on economic activities and is less detailed than the combined nomenclature (CN) used for import/export database (Comext), which is based on commodity groups. The PRODCOM data, however, have the advantage that it is possible to estimate the consumption in the country because both import/export and production are provided for the same groups of products. For some of the product groups (where relevant), the data by PRODCOM classification were supplemented with data on import/export by combined nomenclature (CN) commodity codes extracted from the database of Statistics Denmark. For printed matter, production, import and export statistics were not available from the statistical bureaus, but some indicators were available from the Graphic Association of Denmark.

Further data collection on the use in consumer products

Besides the contact with Danish trade organisations and companies' participation in the advisory group, contact was established with Danish trade organisations and companies per e-mail and/or phone:

- Dansk Fashion & Textile (trade association for Danish textile and clothing companies)
- The Graphic Association of Denmark (GA)
- Airline SH-Profile (textile printing company)
- Bestseller A/S

- Kemotextil A/S (textile dye-works)
- Skandinavisk HTP (textile printing company)
- Wacker Kemi (chemical supplier of binders)
- Technological Institute
- Bodo Møller Kemi

Identification of relevant consumer products with potential for releases
Relevant consumer products exempt from the Danish Nanoproduct Register, with the potential for consumer exposure and releases to the environment, were identified on the basis of the authors' general knowledge of the products, the Danish EPA's surveys of consumer products and other literature.

Emission Release Categories - For the standardized supply chain communication of environmental assessments under REACH, a number of EU industry sector groups and trade associations have developed Specific Environmental Release Categories (SPERCs) which describe typical operational conditions that are relevant with regard to the emissions of substances to the environment (CEFIC, 2012). SPERCs for consumer use of relevant products are applied for indication of the potential releases caused by use of the products.

2. Pigments *vis-à-vis* the definition of nanomaterials

2.1 The European Commission's definition of nanomaterials

In October 2011, the European Commission published a Commission Recommendation on the definition of nanomaterial (2011/696/EU).

The Recommendation defines that:

- *"'Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm."*

It should be noted that according to the preamble of the definition, the definition pertains to the constituent particles and therefore not to the size of the agglomerates/aggregates. Constituent particles are sometimes referred to as "primary particles" and this term is used in this report as well.

Agglomerates and aggregates are defined as follows:

- *"'agglomerate' means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components*

- *'aggregate' means a particle comprising of strongly bound or fused particles".*

Where technically feasible and requested in specific legislation, compliance with the definition may be determined on the basis of the specific surface area by volume. In this situation, the sample is a "nanomaterial" when the specific surface area by volume is greater than 60 m^2/cm^3. The recommendation specifies that a negative result according to this criterion would not overrule a positive classification from particle size analysis.

In relation to analytical methods for determining size distribution and specific surface area, the recommendation notes in the preamble the following: "*Measuring size and size distributions in nanomaterials is challenging in many cases and different measurement methods may not provide comparable results. Harmonised measurement methods must be developed with a view to ensuring that the application of the definition leads to consistent results across materials and over time. Until harmonised measurement methods are available, best available alternative methods should be applied."*

It should be noted that the EU nano definition is up for review at the end of 2014. According to the Recommendation, the review should particularly focus on whether the number size distribution threshold of 50 % should be increased or decreased. This project is based on the current definition.

2.2 Introduction to pigments

In recent years, Eurocolour has been involved in the discussion of pigments *vis-à-vis* the definition of nanomaterials and, in this context, has published the report "Nano. The measure of all things" (Eurocolour, 2012), which provides an introduction to pigments and information of relevance for the discussion of nanosized pigments. Furthermore, ETAD published a position paper on organic pigments and nanomaterials in 2009. Both papers, together with information from the Chemical Encyclopaedia and manufacturer's websites form the basis for the following section.

2.2.1 The mechanisms of the pigments and dependency on size

The colour of a pigment can be brought about in different ways, depending on how the pigment interacts with the visible part of the light spectrum or generates light in this part of the spectrum.

According to Ullmann's Encyclopaedia of Industrial Chemistry (2000), inorganic pigments can be classified based on their interaction with the light as follows (the same mechanisms will apply to organic pigments):

- **White pigments**: The optical effect is caused by <u>nonselective light scattering</u> (examples: titanium dioxide and zinc sulfide pigments, lithopone, zinc white)
- **Coloured pigments**: The optical effect is caused by <u>selective light absorption</u> and also to a large extent by <u>selective light scattering</u> (examples: iron oxide red and yellow, cadmium pigments, ultramarine pigments, chrome yellow, cobalt blue)
- **Black pigments:** The optical effect is caused by <u>nonselective light absorption</u> (examples: carbon black pigment, iron oxide black)
- **Lustre pigments**: The optical effect is caused by <u>regular reflection or interference</u>
- **Metal effect pigments:** <u>Regular reflection</u> takes place on mainly flat and parallel metallic pigment particles(example: aluminium flakes)
- **Nacreous pigments:** <u>Regular reflection</u> takes place on highly refractive parallel pigment platelets (example: titanium dioxide on mica)
- **Interference pigments**: The optical effect of coloured luster pigments is caused wholly or mainly by the phenomenon of <u>interference</u> (example: iron oxide on mica)
- **Luminescent pigments:** The optical effect is caused by the capacity to <u>absorb radiation and to emit it as light of a longer wavelength</u>
- **Fluorescent pigments**: <u>Light of longer wavelengths is emitted after excitation without a delay</u> (example: silver-doped zinc sulfide)
- **Phosphorescent pigments**: <u>Light of longer wavelengths is emitted within several hours after excitation</u> (example: copper-doped zinc sulfide)

The colour of the pigment (including black and white) is a result of the interaction between the pigment and the visible light of a wavelength of 400-700 nm (in air); the pigment may interact differently with radiation of shorter wavelengths (UV-light) or higher wavelengths (infrared light). A white pigment such as titanium oxide, with nonselective light scattering in the visible part of the spectrum, may well absorb light of shorter wavelength.

For the different uses of pigments, specific, individual properties are required, e.g. dispensability, colour intensity, light- and weather-fastness, mechanical resistance, colour shade, transparency or opacity/hiding power. These properties depend on both the chemical composition and the sizes and shapes (morphology) of the pigment particles. To be effective in their applications, the pigments need to be finely dispersed into binders. Examples are the manufacture of printing inks, coloured coatings, polymers or other pigmented materials (Eurocolour, 2012).

The colour intensity, colour shade, and transparency or opacity/hiding power of pigments are determined by the balance between light scattering and absorption. For the individual pigment, these properties are a function of the size and morphology of the particles of the pigment. When the particle size of the pigments is small compared to the wavelength of the light (which for visible light is approx. 400-700 nm, the interaction with the light changes dramatically, in particular as concerns the light scattering.

Opacity - Some pigments are used to provide opacity to a transparent or translucent surface. The amount of opacity that is provided is a function of the refractive index difference between the pigment and the medium in which the pigment particles are dispersed. The multiple light scattering in the pigment–medium interface results in light only interacting with the top surface of an object, which therefore controls its colour. This property is especially important in thin films, such as paints, where the goal is to hide the original colour of the object. According to Kirk Othmer (2005), a pigment with a particle size between 160 and 280 nm gives the maximum dispersion of visible light. The manufacturer BASF (2014) indicates that inorganic pigments have a much larger average particle size than organic pigments and the optimum particle size needed to achieve maximum light scattering – resulting in opacity – is between 400 and 800 nm. The particles sizes of inorganic pigments are much closer to this optimum than those of organic pigments, which tend to be much lower. This is the main reason why most organic pigments are considered transparent and most inorganic pigments opaque (BASF, 2013). It should be noted that the particle size referred to here is the size of the aggregated and agglomerated particles and not the primary particles.

Transparency and colour strength - When the particle size of the pigment is sufficiently small as compared to the wavelength of the light coatings pigmented with the pigments become transparent (the exact size depends e.g. on the refractive index of the pigment). The absorption will still take place but the non-absorbed light is not scattered, but penetrates the matrix. The particle size also influences the colour strength (the facility with which a coloured pigment maintains its characteristic colour when mixed with another pigment). According to ETAD (2009) for colouristically strong organic pigments there is a very marked dependence of optical properties on particle size; the maximum colour strength occurs when the particles in the final application media are approximately one twentieth of the wavelength of light (i.e. in the range of approximately 20-35 nm). This size also gives highly transparent systems, which for example in the printing industry is desirable. In the last two decades much of the research and development work has concentrated on producing very small particles, which were referred to as sub-micron particles some years ago, but which the industry has since designated “nanoparticles” (ETAD, 2009).

Examples - The differences in the median particle size between pigments providing opacity and transparency appear clearly from the catalogues from major manufacturers of pigments. Please note that the particle size is the size of the actual particles (which may be aggregates and agglomerates) and not the size of the primary particles as discussed later in this chapter.

Transparent pigments are used for various applications such as some automotive paint, wood finishes, artist's colours, industrial coatings, some plastic applications, cosmetics and inks.

One example is Clariant's product range "Selected pigments for wood coatings". The pigments for the application area "Opaque pigments for lead-free pigmentation" typically have a median particle size in the 250-400 nm range, whereas the "Transparent pigments for decorative shade effects" have a median particle size of 40-75 nm (Clariant, 2014a). For the transparent wood stains, the manufacturer markets the products series "Hostafine"® with 15 pigments, all with a median particle size of less than 100 nm. (Clariant, 2014b).

Conclusion
Whereas many pigments unintentionally may contain a fraction of the particles in the nanosize (as discussed further in the next chapter), many pigments for applications where high colour strength and transparency is desired are intentionally manufactured with a particle size distribution which clearly identifies them as nanomaterials. The same pigments may be used for different applications

and the particle size distributions of two different commercial products based on the same pigment may differ significantly.

The applications of nanosized pigments are further described in Chapter 0.

2.2.2 Manufacture of pigments and size distribution

As discussed in the previous section, the average size of the pigments to some extent depends on the actual application of the pigment.

To be effective in their applications, the pigments need to be finely dispersed into binders. A pigment consists of a large number of small to very small particles, which are either generated in comminution (downsizing) processes in mills or comparable powdering devices or synthesized as crystals in a suspension. Ideally, it is desirable for all particles to be of similar sizes, but this is not possible in practice. Therefore, differently sized particles are invariably obtained in the manufacture of pigments. The following briefly describes the various manufacturing processes as extracted from Eurocolour (2012) if nothing else is indicated.

Organic pigments

Organic pigments are manufactured in chemical syntheses which frequently comprise several process steps, where starting materials react with each other to form a new compound.

Even very complex structures can be produced in relatively few stages. Where necessary, these structures are additionally modified chemically – e.g. to bring about a different shade of the same colour or to optimise certain properties of the pigment for its intended use.

The processes result in the formation of small, solid pigment particles. After the reaction these pigment particles need to be separated from the solution. For this purpose, solvents may be used, other treatments added or, quite simply, the solid can be filtered out – depending on the substance class.

The manufacturing is illustrated in Figure 1. As described above, the pigments may be synthesised as coarsely crystalline crude pigments which are ground in order to obtain fine-sized pigments, or they may be synthesised as amorphous pigments in suspension which are grown into the final size. In both cases the result is agglomerates and aggregates of the primary particles in suspension. The primary particles would typically be of a size meeting the EU nanoparticle definition, and thus the pigment would fulfil the EU nano definition. The suspension is dried and a pigment powder is generated. The median size of the dried pigments is typically much larger than the median size of the primary particles. Depending on the application, the powder is subsequently - by the introduction of energy - suspended in a liquid. If small particle size is requested, high shear [2] forces are introduced in order to break the agglomerates and aggregates apart. Pigments with the same primary particle size may thus be used for different suspensions with different particles size distributions.

The equipment used to manufacture the fine-sized pigments ("nanopigments") may be the same as used in the manufacture of other nanomaterials. An example is the Nanomill Zeta® RS (Netzcsh Group, 2013) which is marketed for manufacture of e.g. pigments for LCD and pigments for inkjet, photo catalyst titanium oxide (TiO_2), nano-silicium oxide (SiO_2) for paper and nano-zinconium oxide (ZrO_2) for electronics. The equipment may be used not only for dispersion of agglomerated nano-scale pigments (as described in the figure below), but also for a one-step comminution (grinding) of the pigments in dispersion.

[2] Shear forces are unaligned forces pushing one part of a particle in one direction, and another part of the particle in the opposite direction.

All the manufacturing methods described here can be followed by further process steps to optimise the technical properties of the pigment needed for its application, especially dispersibility and hiding power but also colour shade or weather-fastness. For organic pigments, after-treatment can take the form of heating in the presence of solvents and/or chemical additives.

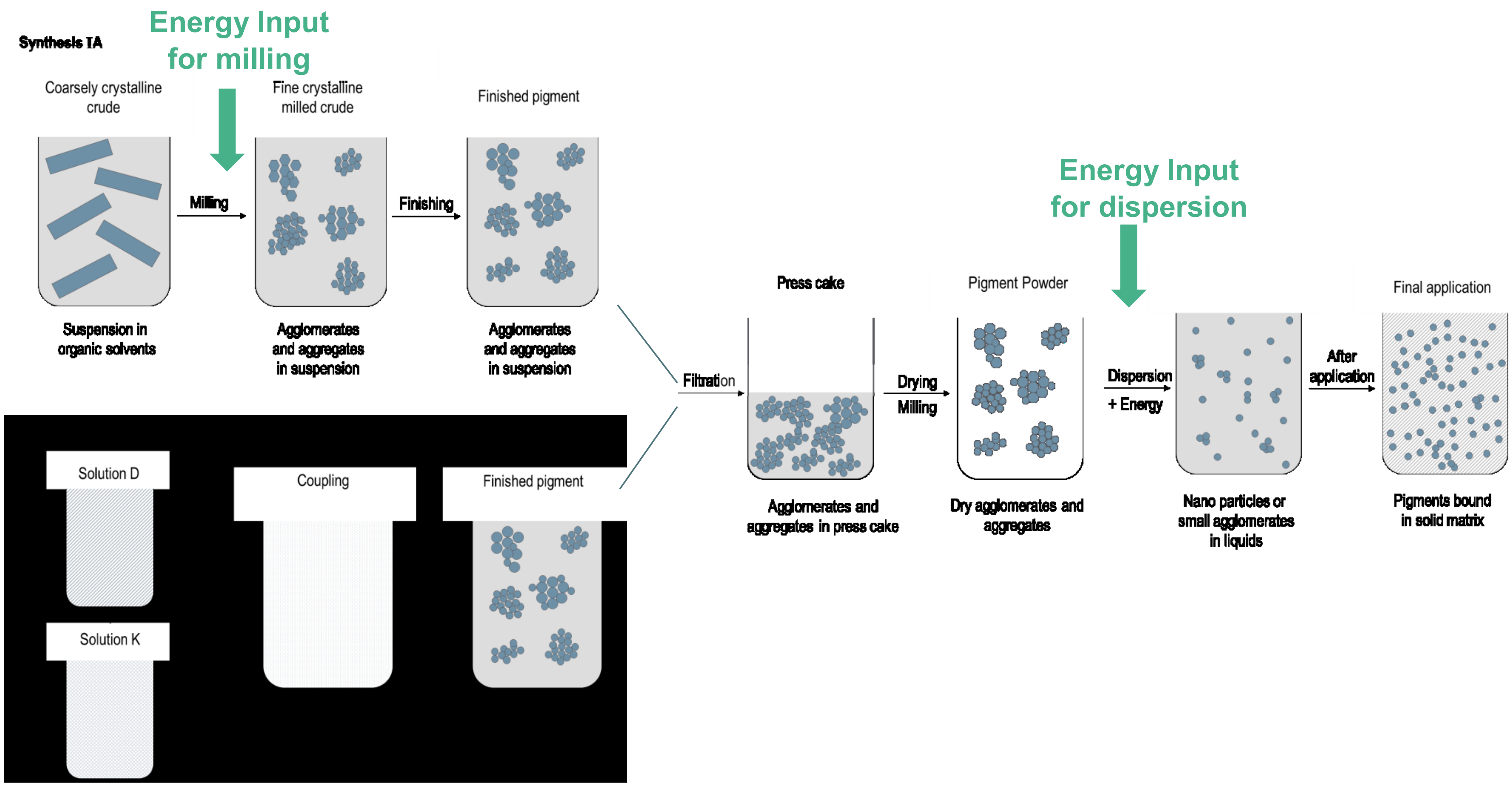

FIGURE 1
PROCESSES FOR MANUFACURING OF ORGANIC PIGMENTS (KUND, 2014)

Inorganic pigment
The following description for inorganic pigments is mainly based on Kirk Othmer (2005). For inorganic pigments, synthesis generally takes place through heat treatments (thermal processes) in rotary kilns or in other calcining processes. Depending on the choice of the raw material, there can be combinations of precipitations and thermal processes where different colour shades or certain optical effects need to be achieved. One of the oldest white pigments is calcium carbonate, which is obtained in several stages starting with the calcining of limestone.

Precipitation - At the beginning of the precipitation process, solid raw materials are dissolved and blended with each other. Depending on the manufacturing method, further substances may be added; for example, acids or bases. All these substances in the liquid react with each other and create the desired new substance, which forms as a solid. Crystals of this solid start to form on so-called seed dispersions. Crystals grow on these nuclei and can then be separated from the solution, e.g. by way of filtration. After separation from the liquid, the solid particles are washed and dried, using e.g. spray driers or belt driers.

Where the particle size is required to be as homogeneous as possible, the material is processed, for example, through a classifier. Depending on intended uses of the pigment, further purification or processing steps can follow.

The processes described are used in the manufacture of e.g. inorganic colour pigments, including iron oxide (red, yellow or black), bismuth vanadate (yellow), ultramarine pigments or iron blue pigments. The same goes for titanium dioxide (a white pigment with good hiding power for a very wide range of applications) and synthetic amorphous silica.

Precipitation onto a substrate is one variation of the precipitation process: prior to the chemical reaction intended to lead to precipitation, minute insoluble particles are introduced into the solution. Next, the desired crystals accumulate in a thin, defined layer on the surfaces of these particles.

As soon as the desired layer thickness is reached on the carrier particle, the reaction is stopped and the solid is separated from the solution.

Metal effect pigments
The basic material for the manufacture of metal effect pigments is the respective metal or can also be an alloy. Two processes are used:

Flamespraying - The molten metal is squeezed through a nozzle and as the jet cools, a granule with particle size dimensions in the micrometre range (i.e. above nano-range) is formed. This granule is ground into thin, platelet-shaped pigment particles to bring about the desired properties of the pigment.

Grinding - The duration and intensity of the grinding process influence the particle size distribution as well as particle thicknesses and improve other properties required of the pigments. Either during grinding or subsequently, the particles of the pigment are polished – i.e. a layer is applied to prevent caking or welding together. Metal pigments are placed on the market almost exclusively in dust-free forms, e.g. pastes or suspensions.

2.3 Determination of particle size *vis-à-vis* the definition
Until now, no guidance has been published on analytical method or methods to apply in relation to determining particle size distributions or surface area *vis-à-vis* the EU definition.

The European Commission Joint Research Centre (JRC) has looked further into the issue and published the report *Requirements on measurements for the implementation of the European Commission definition of the term "nanomaterial"* (Linsinger *et al.*, 2012). This report focuses on the requirements for particle size measurements of nanomaterials based on the definition and discusses capabilities of measurement methods currently available. Two illustrative examples (silica and zinc oxide nanoparticles) are elaborated, but otherwise no nanomaterial specific cases are addressed.

The report, *inter alia*, concludes that:

- *"Summarising the current technical limitations, none of the currently available methods can determine for all kinds of potential nanomaterials whether they fulfil the definition or not. Therefore, a range of measurement methods is required to investigate whether nanomaterials fulfil the regulatory definition. Implementation of the definition via measurements poses significant difficulties for polydisperse materials and is currently usually not possible for aggregated materials if the size distribution of their constituent primary particles must be determined, unless the aggregates as particulate materials themselves fulfil the nanomaterial definition",* and
- *"If a rapid implementation of the definition through measurements is needed, dedicated guidance documents will have to be provided for specific materials and sectors, with clear and justified indication of the relevant particle size measurement methods and test conditions",* and
- *"A combination of several methods, ideally supported by information on the manufacturing process of the material under investigation, will have to be employed for robust assessment*."

At the EU level, the recently initiated EU 7th Framework Programme project "NanoDefine" has been initiated to support implementation of nano legislation based on the EU nano definition by (http://www.nanodefine.eu/index.php/project-overview):

- addressing the issues on the availability of suitable measuring techniques, reference material, and validated methods acceptable for all stakeholders (authorities, policies, industries), and
- an integrated and interdisciplinary approach and close international cooperation and networking between academia, concerned industries and standardization bodies.

The NanoDefine project is a 29-partner consortium of European Research, Technology and Development Performers (RTD Performers), metrology institutes, and nanomaterials and instrument manufacturers.

More specifically, the NanoDefine project aims at developing validated, robust, readily implementable and cost-effective measurement methods capable of reliably measuring the number concentration with focus on the 1-100 nm range, and to develop a decision framework and guidance for determining whether a sample is a nanomaterial or not.

It should be noted that NanoDefine refers to e.g. "decision framework", "implementable" and "cost-efficiency". One of the key reasons for this is that, by and large, more sophisticated and expensive methods such as TEM/SEM (Transmission/Scanning Electron Microscopy) give more accurate results e.g. in relation to constituent particles, whereas methods frequently applied by industry such as e.g. Light Diffraction and DLS (Dynamic Light Scattering) are much cheaper but with less precision/dissolution of results. However, if these cheaper methods could be used at a screening level to determine whether a material is nano or not, and/or used in a weight-of-evidence approach, it could potentially increase cost-efficient testing of a wide range of materials.

2.3.1 Particle size distribution of pigments

All pigments contain particles of different sizes. Dispersed in a medium, they are designated "polydisperse" materials. How the sizes of the individual particles vary is described by the particle size distribution.

As the primary particles have a tendency to aggregate and agglomerate, measuring the particles size distribution of primary particles is challenging.

Primary particles, aggregates, agglomerates and flocculates
Pigments are morphologically described by a standardized terminology; they can occur as single, constituent or primary particles, aggregates, or agglomerates. The definitions for agglomerates and aggregated from the Commission Recommendation on a definition of 'nanomaterial' are shown in section 2.1.

Primary particles - The final crystals that ultimately constitute the crude pigment product are known as primary particles. The Commission Recommendation indicates that the 50% number concentration refers to constituent particles. Constituent/primary particles are true single crystals with the typical lattice disorders or combinations of several lattice structures that appear as units under an X-ray (Herbs *et al.*, 2005). Primary particles may be of a variety of shapes, such as cubes, platelets, needles, or bars, as well as a number of irregular shapes. The size of a particle is usually determined by the shortest external dimension.

Aggregates - Aggregates are primary particles that are grown together at their surfaces to form small crystallites. The total surface area of an aggregate is smaller than the sum of the surfaces of the individual particles. Aggregates are not broken down by dispersion processes (Herbst *et al.*, 2005). In practice, the particles in a dispersion consist of a mixture of primary particles, agglomerates and aggregates, and the particle size distribution determined by several analytical methods will be the external dimensions of the primary particles and the aggregates.

Agglomerates - Agglomerates are groups of single crystals and/or aggregates, joined at their corners and edges but not grown together, which can be separated by a dispersion process (Herbst *et al.*, 2005). The surfaces of the individual crystals are readily available to adsorption. By definition, the total surface area of an agglomerate may not differ considerably from the sum of the surfaces of the individual particles. For surface energy reasons, the tendency of the small particles to agglomerate and form crystallites increases with decreasing particle size. This is particularly true for the final phase of pigment manufacture, the drying and milling processes. Pigment powders therefore comprise a mixture of such crystallites and single crystals (Herbst *et al.*, 2005). The dispersibility of a pigment is largely determined by the nature and density of the agglomerates, which in turn depend on particle shape and density.

Incorporation into the application medium, be it a plastic, a printing ink, or a paint, relies on dispersion, which involves an effort to break down the agglomerates as far as possible (Herbst *et al.*, 2005).

Flocculates - Already dispersed pigment particles may for various reasons reassemble and form loosely combined units with various shapes. The most important among these are flocculates, assemblies of wetted crystallites and/or aggregates or smaller agglomerates (Herbst *et al.*, 2005). They usually form in a low viscosity medium which fills the interior cavities of the pigment flocculates. Flocculates are therefore mechanically more labile than agglomerates and can usually be broken up by weak shear such as stirring.

The particle size
The size of the particles is determined by measuring the outer dimensions of the particles and may be represented by the average diameter, the smallest or the longest diameter. The Commission Recommendation refers to "*one or more external dimensions is in the size range 1 nm-100 nm",* i.e. the particle should be represented by the smallest diameter of the constituent particles.

Determination of particle size distribution

The particle size distribution of a pigment powder is usually different from that found when the pigment is dispersed in a medium (designated the pigment-vehicle system); and since both have practical importance, methods were developed for their determination.

The JRC report (JRC, 2012) describes a range of measuring methods: Electron Microscopy (EM), Dynamic Light Scattering (DLS), Centrifugal liquid sedimentation, Small-angle X-ray scattering, Field Flow Fractionation, etc. The report provides a summary table on measurements range and medium, type of size distribution, whether they can deal with challenges of particular types of nanomaterials and whether standards are available.

As mentioned above, agglomerates are preferably broken when the pigment is dispersed in a medium, and measurements of the pigments in suspension gives the most correct measure of the size distribution of the pigments in the final mixtures. Five of the methods measure the size distribution in a suspension. The measurements range of the Field Flow Fractionation goes down to 1 nm, whereas the lower range for the other methods measuring in suspension goes down to 5 to 25 nm. Size analyses are commonly carried out by mixing the pigment powder with an organic solvent (whereby the agglomerates are broken apart) or with water and adding appropriate surfactants to enhance the dispersibility of the powder (Kirk Othmer, 2005). The particles measured in practice will be a mixture of primary particles, agglomerates and aggregates when using the routine methods.

Technical documentation of the commercial products (e.g. as appearing on the websites of companies) generally does not indicate the method applied for the indicated particle size distributions.

Representation of particle size distribution

The particle size distribution can be represented by three different types of distribution, illustrated in the following figure:

- **Numerical Distribution** n(D), the percentage of particles with a given equivalent diameter. referred to in the Commission Recommendation as the "number size distribution";
- **Surface Area Distribution** s(D), the percentage of particles with a certain surface area plotted against the equivalent diameter;
- **Volume or Mass Distribution** v(D), the percentage of particles with a certain volume or mass, respectively, plotted against the equivalent diameter.

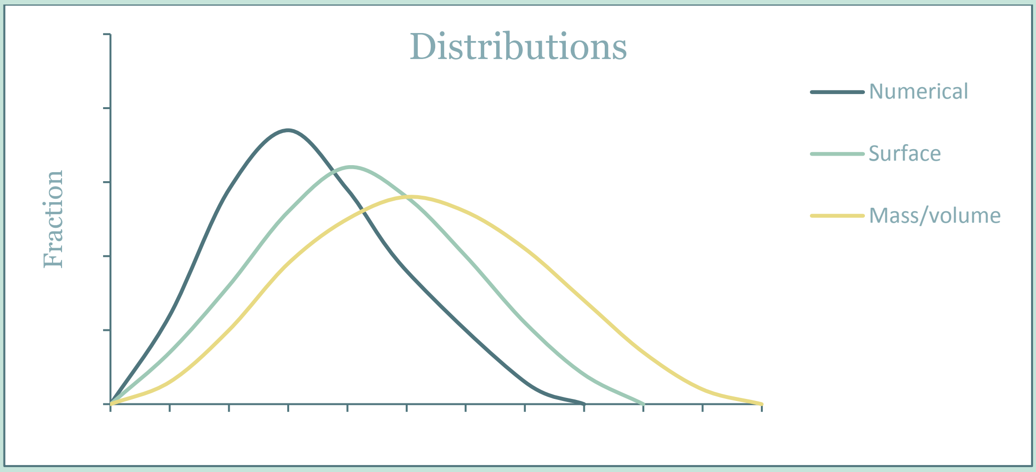

FIGURE 2
NUMERICAL DISTRIBUTION, SURFACE DISTRIBUTION AND MASS DISTRIBUTION.

The majority of the REACH registrations of the pigments include information on the volumetric size distribution of the pigment powder e.g. different percentiles in the distribution such as D10, D50 (median value) and D90, expressed as the mean diameter of the particles. The median value of the volumetric size distribution is much higher than the median value of the numerical distribution (used for the nano definition) as the main part of the mass is bound in the larger particles. It is not possible to calculate the median value of the numerical distribution from the volumetric size distribution, and the data on particle size distribution in most of REACH registrations are thus of little relevance as to the determination of whether the substances can be considered as nanomaterials.

The size distribution can be represented by various parameters:

- The **arithmetic mean value** is the average of all sized measured.
- The **modal value** is the most frequently occurring size in the distribution (top point in the distribution);
- The **median value**. The median is the 50% percentile of the distribution where 50% of the particles are smaller than the value.

In the technical specifications of commercial products, the particle size distribution is usually represented by the median (D_{50}) of the volumetric size distribution. Some specifications use the term "average particle size" which may indicate that the value is the arithmetic mean, but it more likely represents the median.

The median value is always lower than the arithmetic mean, which is of importance in the interpretation of the available parameters *vis-à-vis* the nano definition. If the mean value is below 100 nm, the median value will similarly be below 100 nm (how much more depends on the distribution).

Similarly, if the mean or median of the volumetric/mass distribution is below 100 nm, the median of the numerical size distribution will always be below 100 nm.

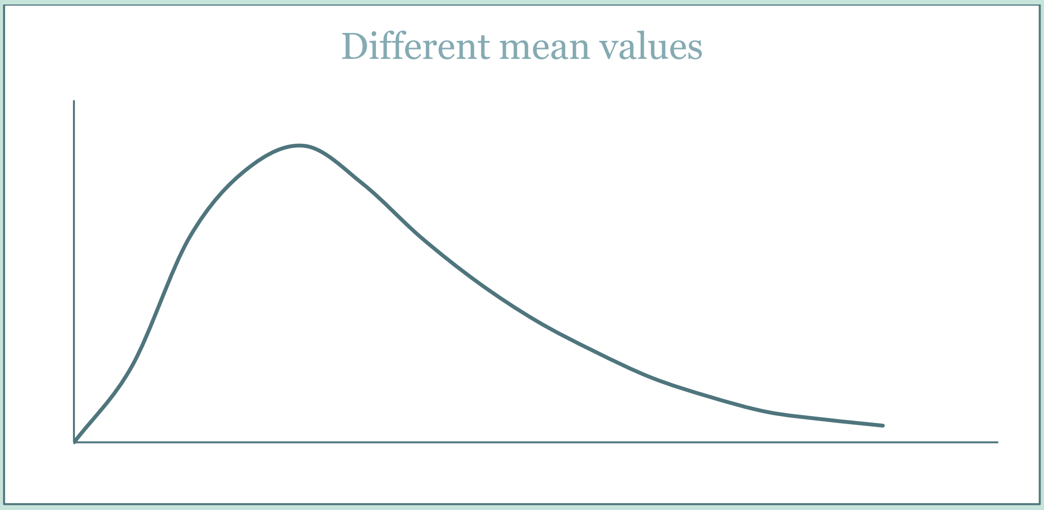

FIGURE 3
DIFFERENT MEAN VALUES FOR THE PARTICLE DIAMETER *D*.

Two examples of number size distributions determined by transmission electron microscopy (TEM) of a sample of Pigment Yellow 83 are shown below. The upper part of the figure (A) shows the distribution of the pigment in a dispersion after extreme shear forces have been introduced. The lower figure (B) shows the distribution of the same pigment in a standard paint dispersion. The median diameter of the upper distribution is 34 nm (a "nanopigment") whereas, in the lower distribution, it is 134 nm.

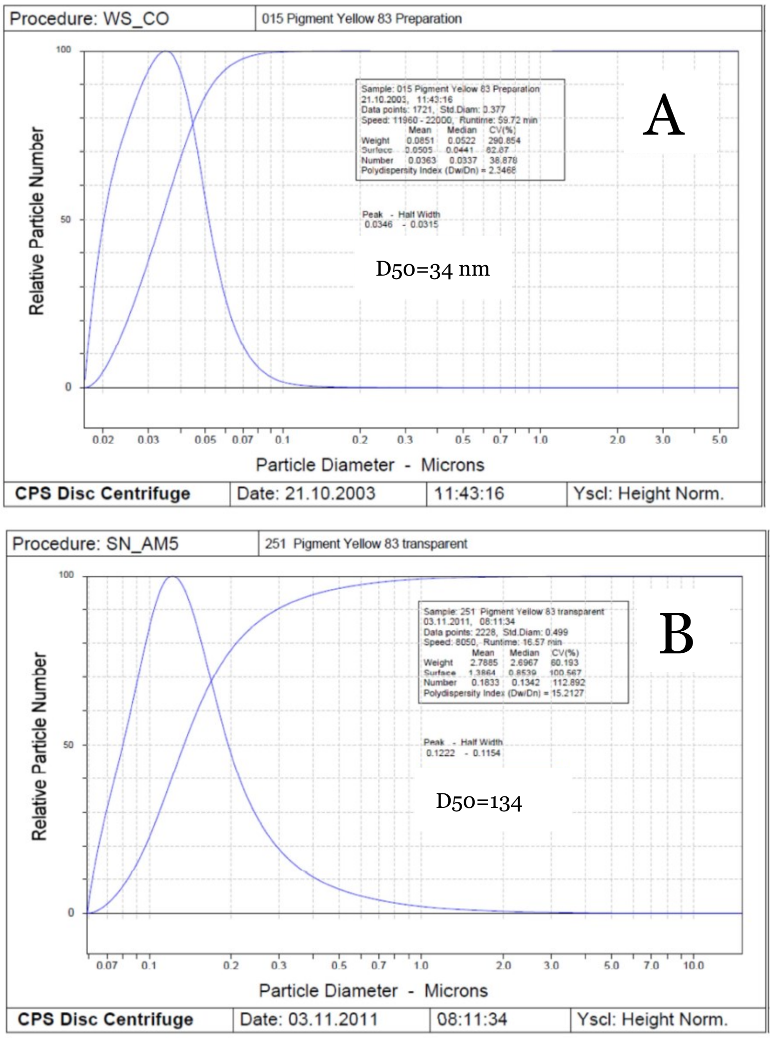

FIGURE 4
TWO EXAMPLES OF NUMBER PARTICLE SIZE TEM ANALYSIS OF PIGMENT YELLOW 83. THE UPPER FIGURE (A) SHOWS THE DISTRIBUTION OF THE PIGMENT IN A DISPERSION AFTER EXTREME SHEAR FORCES HAVE BEEN INTRODUCED. THE LOWER FIGURE (B) SHOWS THE DISTRIBUTION OF THE SAME PIGMENT IN A STANDARD PAINT DISPERSION. PLEASE NOTE DIFFERENT PARTICLE DIAMETER SCALES. (BASED ON KUND, 2014).

Specific surface area

As noted, the JRC report addresses particle size measurement. In relation to the alternative criterion, surface area measurement is typically performed by the Braunauer, Emmett, and Teller method (BET) that measures absorption onto a surface (Kirk Othmer, 2005). This technique gives one number, typically reported in square meters per grams (m^2/g), and does not describe the shape or distribution of particle sizes in the sample (Kirk Othmer, 2005). Typical values for organic pigments range between about 10 and 130 m^2/g (Herbst *et al.*, 2005). The surface area of a pigment, however, is not a definitive value: it is controlled by factors such as the method of determination and the experimental parameters. According to Herbst *et al.* (2005), it appears reasonable to conclude that experimentally determined specific surface areas can only qualitatively relate to the physical characteristics of organic pigments. Instead, their value emerges in combination with other physical or physico-chemical parameters, or in the context of application properties such as oil absorption or wettability.

For the definition of nanomaterials, the Commission Recommendation uses a limit value for the specific surface area in the unit m^2/cm^3. As the surface area in technical documentation is usually provided in m^2/g, it is necessary to calculate the surface area in m^2/cm^3 by multiplying the specific gravity (in g/cm^3) by the surface area in m^3/g. The specific gravity is the gravity of the solid particles and not of the powder, and this property is usually provided in technical data sheets or similar technical documentation.

As noted in Section 2.1, the particle size distribution criterion in the EU nano definition generally overrules the surface area criterion.

2.4 State of the activities addressing pigments *vis-à-vis* the EU nano-definition

Specifically for pigments, a number of activities are on-going in relation to determining whether individual pigments would meet the EU nano definition.

Over the past years, Eurocolour and JRC (European Commission Joint Research Centre) have run a joint activity measuring particle size of a number of pigments with various analytical methods and in various laboratories. Results from these activities are currently confidential but will be reported.

The FP7 NanoDefine project addresses pigments in a dedicated activity. As noted, no results are so far available from this project, but will be included to the extent they are made available to the current project.

In its 2012 Annual Review, ETAD (The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers) notes that "The nano issues" are receiving increased attention, a situation caused *inter alia* by the October 2011 EU nano-definition and the French nano-register. It is stated that: "*While there is general acceptance that many of our products have a significant nano fraction, there is no unanimous agreement as to whether they are nanomaterials as defined; the situation being made more complex as there is as yet no officially recognised method for the determination of size distribution based on particle number*. ETAD has established a Nano Steering Committee (NSC)."

2.5 Summary of particle size distribution and parameters

According to information from industry, most pigments are likely to meet the EU nano definition based on the size of the primary particles. Even when the final products are intended to have a larger particle size, it is common to grind the pigments into smaller primary particles, which subsequently aggregate and agglomerate into larger particles. By this process, it is possible to obtain a more uniform particle size distribution as compared to a manufacturing process where the pigments were ground into larger particles. Pigments with intended larger particle sizes might also often contain a "nanotail", which is low in mass, but easily contributes more than 50% of the particle number, which would trigger that the pigment falls within the nano definition. The subsequent dispersion of the aggregated and agglomerated particles in the dispersion media determine the particle size of the final product.

Whereas it appears that most pigments consist of primary particles, rendering the pigment to fall within the EU nano definition; for any assessment of exposure to the pigments it may still be relevant to consider the actual size distribution of the pigment particles in the suspension media.

As discussed in the previous chapter, it is challenging to determine that a pigment is <u>not</u> a nanomaterial on the basis of the generally available measured parameters, whereas it can be concluded that most pigments most likely can be considered nanomaterials. If, based on available information provided by manufacturers in the technical data sheets and similar product documentation, a pigment falls within the definition of nanomaterials, it will be assumed that the pigment is a nanomaterial in this context. All other pigments are considered as "possible nanomaterials". Based on the findings in this project, most of the latter are most likely nanomaterials according to the EU nano definition.

The following information on the pigments may be relevant for the determination of whether the pigments may be considered pigments in the nanosize.

Particle size distribution

- Preferably the particle size distribution is indicated as the median value of the numerical particle size distribution. It will be assumed that the number of particles below 1 nm is insignificant and in this case, the pigment is considered a nanomaterial if the median of the numerical distribution is below 100 nm. According to the JCR report, in practice, particles are larger than 1 nm (Linsinger *et al.*, 2012).
  - When only a single number is given, it is important to note whether this is a median, average, mean or mode. As the arithmetic mean in the typical distribution is higher than the median, the pigment is considered a nanomaterial if the arithmetic mean of the numerical distribution is below 100 nm.
  - When a particle size distribution is given, it is important to note whether this refers to particle numbers or mass. Mass or volume particle size distributions are of limited use as it is not possible to recalculate to the numerical particle size distributions. However, if the mass distribution indicates that >50% of the mass is below 100 nm, the pigment is clearly a nanomaterial.

Specific surface area per volume

- Preferably the specific surface area is indicated as the specific surface area per volume unit.
  - In most cases the specific surface area is provided per mass unit (as BET [3]). The specific surface area per volume may be calculated from the specific surface area per mass and specific density of the pigment.
- Any available data about agglomeration/aggregation state of the pigment.

[3] BET: Surface area measurement performed by the Braunauer, Emmett, and Teller method

3. Applications and market of pigments

3.1 Global market of pigments

Data on the global market of pigments are usually divided between the inorganic and organic pigments. As the titanium dioxide (TiO2) in itself takes up about half of the total tonnage, this pigment is often addressed separately.

3.1.1 Inorganic pigments

Titanium dioxide (TiO_2)
Titanium dioxide is by far the most used pigment by the industry. In 2012, the estimated worldwide production of titanium dioxide was approximately 8.6 million tonnes. This was comprised of 7.8 million tonnes was the mineral ilmenite and leucoxene and 0.8 million tonnes rutile (Bedinger, 2014).

The majority of the titanium dioxide was used for the manufacture of pigments. World titanium dioxide pigment capacity in 2013 was estimated at 6.6 million tonnes (USGS, 2014). Titanium dioxide pigment is mainly used in the production of paints and lacquers (~50%), plastics (~20%), and paper (~20%) (Kirk Othmer, 2005). Other applications include the pigmentation of printing inks, rubber, textiles, leather, synthetic fibres, glass enamel, white cement, roofing granules, and cosmetics (Kirk Othmer, 2005). Non-pigmentary applications include the production of glass, ceramics, electroceramics, catalysts, and as raw material to form mixed-metal oxide pigments.

Carbon black - Although carbon black consists of carbon, it is by convention considered together with the inorganic pigment (Kirk Othmer, 2005). Worldwide carbon black consumption in 2010 was 9 million t/y and was expected to reach 13 million t/y 2015 (Smithers Apex, 2010). Globally, approximately 90% of the carbon black produced is used in the rubber industry as a reinforcing filler in tyres and a variety of other products. About 9% (~0.8 million t/y) of global consumption is used as black pigment in other industrial sectors like plastics, paints, varnishes and printing inks. The remaining 1% is used in hundreds of diverse products (Environment Canada, 2013).

Other inorganic pigments
Among the other inorganic pigments, the iron oxides account for the most significant portion. The global market for iron oxides in 2013 is estimated at 1.1 million tonnes, whereas the total tonnage for all other inorganic pigments is estimated at 0.7 million tonnes (MarketsandMarkets, 2013).

The global market for inorganic pigments (excl. titanium dioxide) by application area is shown in Table 1. The total tonnage is increasing.

Construction - Pigments (excluding TiO2) for construction account for approximately 50% of the market. The pigments are used for colouring concrete, mortar, tiles, lime, plaster, etc. The building elements are coloured walls, concrete structures, floors, etc. Pigments used for construction are mainly the iron oxides, which are further described below.

Other applications - Other major application areas are coatings (26% of total), plastics (8%) and paper (5%).

TABLE 1
GLOBAL MARKET FOR INORGANIC PIGMENTS EXCL. TITANIUM DIOXIDE BY APPLICATION AREA (MARKETSANDMARKETS, 2013)

Application	Market consumption, 1000 tonnes			
	2011	2012	2013	2013, percentage of total
Construction	863	890	918	51%
Coatings	443	455	468	26%
Plastics	131	137	144	8%
Paper	81	85	90	5%
Others	161	170	180	10%
Total	1,678	1,738	1,800	100%

Iron oxides pigments
Iron oxide is the next most used inorganic pigment with an estimated worldwide consumption in the year 2013 of 1.1 million metric tons. Iron oxides can be produced by the beneficiation of naturally occurring materials or synthetically from iron salts. In 2005, natural iron oxide pigments accounted for about 37% of the total iron oxide pigment use while synthetic iron oxides accounted for about 63%. The main advantage of the natural iron oxide pigments, as compared to the synthetic ones, is their low cost (Kirk Othmer, 2005).

As shown in Table 2, about 54% of the iron oxide pigments are used to colour cement and other construction materials, and about 24% is consumed in the production of coatings (mainly paints). For colouring plastics and rubber, synthetic iron oxide pigments are preferred and plastics and paper take up some 6% and 3%, respectively.

TABLE 2
GLOBAL MARKET FOR IRON OXIDE PIGMENTS EXCL. TITANIUM DIOXIDE BY APPLICATION AREA (MARKETSANDMARKETS, 2013)

Application	Market consumption, 1000 tonnes			
	2011	2012	2013	2013, percentage of total
Construction	550	569	570	54%
Coatings	238	249	253	24%
Plastics	59	62	63	6%
Paper	28	30	32	3%
Others	135	138	137	13%
Total	1,010	1,048	1,056	100%

3.1.2 Organic pigments
The global market for organic pigments totals about 0.5 million tonnes in 2013 (Table 3) corresponding to approximately 6% of the global pigment market. The major application area was print-

ing inks (60% of the total), coatings (18%) and plastics (11%). The remaining 11% are used for a wide range of different applications.

TABLE 3
GLOBAL MARKET FOR ORGANIC PIGMENTS BY APPLICATION AREA (MARKETSANDMARKETS, 2013)

Application	Market consumption, 1000 tonnes			
	2011	2012	2013	2013 percentage of total
Printing ink	268	284	300	60%
Coatings	82	86	90	18%
Plastics	51	53	55	11%
Others	50	476	55	11%
Total	451	476	500	100%

Different systems for classification/grouping of the organic pigments are applied either by chemical constitution or by coloristic properties. In market surveys both systems are used.

The organic pigments may be divided into different types of pigments on the basis of their chemistry (Ullmann's, 2000a):

- Azo Pigments
  - Monoazo Yellow and Orange Pigments
  - Disazo Pigments
  - β-Naphthol Pigments
  - Naphthol AS Pigments (Naphthol Reds)
  - Azo Pigment Lakes (Salt Type Pigments)
  - Benzimidazolone Pigments
  - Disazo Condensation Pigments
  - Metal Complex Pigments
  - Isoindolinone and Isoindoline Pigments

- Polycyclic Pigments
  - Phthalocyanine Pigments
  - Quinacridone Pigments
  - Perylene and Perinone Pigments
  - Diketopyrrolo–Pyrrole (DPP) Pigments
  - Thioindigo Pigments

- Anthraquinone Pigments
  - Anthrapyrimidine Pigments
  - Flavanthrone Pigments
  - Pyranthrone Pigments
  - Anthanthrone Pigments

- Dioxazine Pigments

- Triarylcarbonium Pigments

- Quinophthalone Pigments

Azo pigments - Azo pigments account globally for nearly 50% of the total tonnage of organic pigments. Azo compounds are compounds bearing the functional group R-N=N-R', in which R and R' can be either aryl or alkyl groups (Ullmann's, 2000b). Major subgroups are monoazo and diazo pigments. Due to the complexity of their chemical names, azo pigments are rarely referred to by IUPAC or Chemical Abstracts nomenclature. Practical considerations make it more convenient to designate these compounds according to their colour index number.

In the EU (further described in section 3.3) the azo pigment with the highest registered tonnage (10,000-100,000 t/year) is C.I. Pigment Yellow 12 (CAS No 6358-85-6), which is used to a large extent in letterpress and offset printing inks as the yellow pigment in three and four colour printing (Ullmann's, 2000b).

Phthalocyanine - Phthalocyanine is an intensely blue-green-coloured aromatic macrocyclic compound belonging to the group of polycyclic pigments. The phthalocyanine pigments account for about 21% of the global consumption of organic pigments. In this group, C.I. Pigment Blue 15 (CAS No 147-14-8) is the pigment registered with the highest tonnage in the EU (10,000-100,000 t/year). The pigment is used in used in inks, coatings, and many plastics.

Other organic pigments - Pigments belonging to the other groups account in total for some 30% of the global consumption.

TABLE 4
GLOBAL MARKET FOR ORGANIC PIGMENTS, BY TYPES (MARKETSANDMARKETS, 2013)

Type	Market consumption, 1000 tonnes	Percentage of total
	2013	2013
Azo pigments	245	49%
Phthalacyanines (blue and green)	105	21%
High performance and others	150	30%
Total	500	100%

3.2 Overall data for the European pigment market

In the production and import/export statistics from Eurostat, volume data on pigments are confidential.

According to the market survey, the overall data for the European market for pigments are shown in Table 5. Titanium dioxide accounts for approx. 70% of the total pigment market, while the other inorganic pigments account for approx. 25% and the organic for approx. 5%.

TABLE 5
EUROPEAN MARKET FOR PIGMENTS (MARKETSANDMARKETS, 2013)

Application	Market consumption, 1000 tonnes			
	2011	2012	2013	2013 percent-age of total
Titanium dioxide	1,504	1,529	1,560	70%
Other inorganic	513	527	540	24%
Organic	113	117	120	5%
Total	2,131	2,172	2,220	100%

A more detailed breakdown of the European market for the organic pigments is shown in Table 6. The breakdown unfortunately mixes up classification based on chemistry and classification based on colours, and is therefore difficult to interpret.

TABLE 6
EUROPEAN MARKET FOR ORGANIC PIGMENTS (MARKETSANDMARKETS, 2013)

Application	Market consumption, 1000 tonnes
	2013
Phthalo blue and green	32.4
Classic azo reds/lakes and toner	28.8
Diarylide yellows	12.0
Reds and oranges	15.6
Yellows	9.6
Monoarylides	8.5
Others	14.4
Total	120

Breakdown by application area - No data on the European market of organic and inorganic pigments by application area have been available. Most likely, the breakdown of the European market by application area is quite similar to the global market as shown in Table 1 for the inorganic pigment and in Table 3 for the organic pigments.

3.3 Registered pigments

In total, 197 of the substances on the gross list of 573 pigments (see Section xx) were registered by September 2014 (Table 7). For each of the substances in the registration database (ECHA, 2014), the total registered tonnage is indicated with a tonnage band (tonnage per year) with a factor of ten between the lower and the upper limit (1-10, 10-1,000, 1,000-10,000, etc.).

Data on tonnages and registered applications for each pigment are shown in Annex 1. The indicated tonnage is the total registered tonnages; for some of the substances the application as pigment accounts for a minor volume only.

A summary of the number of substances and the total registered tonnage is presented in Table 7.

The total tonnage (incl. non-pigmentary applications) are 2.8-28 million t/y. Compared with the estimate of the market EU volume for pigments of 2.2 million t/y (Table 5), the data indicates that the actual values for the two substances with a registered consumption in the 1,000,000-10,000,000 t/y range should be in the lower part of the range and that a significant part of the registered tonnage may be for non-pigmentary applications. The REACH registration covers import of pigments in mixtures, whereas the market survey includes the pigments on their own only, which could also be an aspect of the explanation for the higher registered volumes.

TABLE 7
OVERVIEW OF NUMBER OF REGISTERED PIGMENTS AND TONNAGES BY SEPTEMBER 2012

Consortium	Number of registered substances	Tonnage (1,000 t/y) *2	Percentage of total tonnage (mean value) *1
Inorganic Pigment (IP) Consortium	28 (+25 by 2018)	35-350	1%
Organic Pigments Consortia	119 (+3 intended)	61-610	2%
Titanium Dioxide Industry Consortium	2	1,000-10,000	35%
Iron Oxides Consortium	5	310-3,100	11%
Zinc Consortium	2	200-2,000	7%
Carbon Black Consortium	1	1,100-11,000 *3	39%
Lead Consortium	8	110-1,100	4%
Other identified pigments *1	35	15-150	1%
Total	196	2,800-28,000	100%

*1 It has not been determined which consortia are responsible for registration of the remaining substance

*2 Total registered tonnage. It is not indicated in the registration how much of the total tonnage is used as pigment.

*3 Consists of a joint registration of 1,000,000-10,000,000 t/y and an individual registration of 100,000-1,000,000 t/y.

3.3.1 Applications of registered pigments

The registered end-use applications of each of the registered pigments are indicated in the table in Annex 1. For pigments registered by the IP (Inorganic Pigment) Consortium, the indication of applications is based on information from the Consortium's website, whereas for the other pigments the information is based on the indicated applications in the registrations. For some pigments, the registering does not include information on end-uses. For those pigments, the table contains empty cells for all use categories.

In the registrations, end-uses are indicated by the Chemical Products Categories (PC) from the REACH use descriptor system (ECHA, 2010). The *Chemical Product Category* characterizes the use of a substance by the type of end-use product (e.g. lubricant, cleaner, adhesive) in which the substance is known to be used. In this context, the Chemical Product Categories have some limitations as construction materials such as concrete, mortar and tiles as well as ceramics are not covered by specific Chemical Product Categories. In some registrations, use in construction materials is described in addition to the listed Product Categories (e.g. indicated as "concrete colouring: mortar colouring, stucco colouring, paver colouring, roofing tile colouring"), but likely this information on products categories - without a Product Category descriptor - is missing in many registrations.

The overall pattern is in accordance with the overall difference between the use of inorganic and organic pigments as indicated by global consumption by application areas in Table 1 and Table 3.

The **inorganic** pigments registered by the IP Consortium are mainly used for paint, plastics, ceramics and construction, while none of the pigments is indicated for use in inks, finger paints or adhesives. The same is the situation for the iron-oxide pigments.

The **organic** pigments registered by the organic pigments consortia are nearly all indicated as used for inks, paints, and plastics or the registering does not include any information on uses. Inks also cover use for textile printing. For a few pigments, the use in finger paints or adhesives is indicated. The pigments are generally not indicated as used for construction materials and ceramics. This is in accordance with the information on the global market in Table 3.

3.3.2 Inorganic pigments

Carbon black - Carbon black is registered with the largest tonnage. As mentioned above, about 9% of the global consumption is used as black pigment in industrial sectors other than rubber production like plastics, paints, varnishes and printing inks (Environment Canada, 2013). If it is assumed that approximately 10% of the EU market consumption is for pigment, the total tonnage for pigmentary use would be 0.1-1.1 million t/y, and the carbon black would account for approximately 6% of the total (if mean values are applied). The market data shown in Table 5, where carbon black is included in the inorganic pigments, indicated that the actual value should be in the lower part of the range.

Titanium dioxide - The total registered volume of titanium dioxide is in the 1-10 million t/y range which is in accordance with the estimates from the market report above (Section xx), that the total market of titanium dioxide for pigmentary use is approximately 1.6 million t/y.

Iron oxides - The total registered volume for three iron oxides used as pigments is 0.3-3.1 million t/y. The three iron (of the five) oxides with a registered tonnage in the 0.1-1 million t/y range each, diiron trioxide, iron hydroxide oxide yellow, and triiron tetraoxide, appear to mainly be used as pigments with other applications accounting for a minor part of the total volume. Considering the estimate for the total European market of other inorganic pigment of 0.5 million t/y and a global market for iron oxides of 1.1 million t/y, the data indicate that the true values are in the low end of the ranges.

Zinc pigments - Two zinc substances, zinc oxide and zinc sulphide, are registered with tonnages in the 0.1 - 1.0 million t/y range. While zinc oxide was originally used as a pigment, at present its most important application is to aid in vulcanizing synthetic and natural rubber. Paint and coating industries are not using zinc white any more as their main white pigment, but it is used as an additive to improve anticorrosion properties, mildew resistance and durability of external coatings. Zinc oxide is also used as a chemical in the production of many mixed metal oxide pigments, particularly spinels (Kirk Ohmer, 2005). Zinc sulfide is used in applications where white colour shade and low abrasivity are required. In printing inks and paints, it also contributes to their stability. Zinc sulfide is mainly utilized for colouring plastics, synthetic fibres, and in the preparation of special coatings, greases and lubricating oils (Kirk Ohmer, 2005). Considering the total European market for inorganic pigments, the registered zinc oxide is most likely used for non-pigmentary applications whereas the true value for zinc sulfide should be in the lower end of the tonnage range.

Lead pigments - A number of lead pigments are registered. Lead monoxide accounts for the major portion with a registered tonnage of 0.1-1 million t/y. Lead monoxide is mainly used for manufacture of lead glass and pigmentary use is very small. Lead pigments showing a significant consumption are orange lead (10,000-100,000 t/y), lead chromate molybdate sulfate red (1,000-10,000 t/y) and lead sulfochromate yellow (1,000-10,000 t/y). They are registered for use as pigments in paints, plastics, ceramics and “other”. The lead pigments all have a harmonised classification, see Section 3.4.

Inorganic pigments registered by the IP consortium - The registered tonnage of the 35 inorganic pigments registered by the IP Consortium totals 35,000-350,000 t/y. The main substances) are chromium iron oxide and chrome antimony titanium buff rutile (10,000-10,000 t/y each).

3.3.3 Organic pigments

More than 100 different organic pigments are registered. As mentioned above, the organic pigments can be grouped either by chemical constitution or by coloristic properties. For the REACH registration, seven organic pigments consortia have been established: Copper Phthalocyanine Pigments, Diarylide Yellow Pigments, Metal Lake Pigments, Quinacridone Pigments and three single substance Organic Pigments consortia. The grouping of the pigments differs from the groupings mentioned above in section 3.1.2 and the data are readily comparable.

As concerns the applications, they are more or less the same for all the groups with the printing ink, coatings (paint, varnishes, etc.) and plastics as the major application areas. As described in Section xx, a few of the pigments are registered in tonnages of 10,000-100,000 t/year, while many pigments are registered in tonnages of 1,000-10,000 t/year. Among the high tonnage pigments are pigments used in letterpress and offset printing inks such as C.I. Pigment Yellow 12 (CAS No 6358-85-6), which is used to a large extent as the yellow component in three and four colour printing.

3.4 Harmonised classification of pigments

The majority of pigments do not have a harmonised classification in accordance with the CLP Regulation (Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures). As discussed later in section 4.1, it is of importance for the interpretation of data from the Danish Productregister whether the pigments have a harmonised classification.

Pigments with a harmonised classification are listed in the table below. The majority of the substances are either lead or cadmium-containing pigments (covered by general harmonised classifications of lead and cadmium substances).

TABLE 8
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
082-010-00-5	lead chromate molybdate sulfate red; C.I. Pigment Red 104; [This substance is identified in the Colour Index by Colour Index Constitution Number, C.I. 77605.]	12656-85-8	Carc. 1B Repr. 1A STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1	H350 H360Df H373** H400 H410
082-009-00-X	lead sulfochromate yellow; C.I. Pigment Yellow 34; [This substance is identified in the Colour Index by Colour Index Constitution Number, C.I. 77603.]	1344-37-2	Carc. 1B Repr. 1A STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1	H350 H360Df H373** H400 H410

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
082-001-00-6	lead compounds with the exception of those specified elsewhere in this Annex		Repr. 1A Acute Tox. 4 * Acute Tox. 4 * STOT RE 2 * Aquatic Acute 1 Aquatic Chronic 1	H360Df H332 H302 H373 ** H400 H410
048-001-00-5	cadmium compounds, with the exception of cadmium sulphoselenide (xCdS.yCdSe), reaction mass of cadmium sulphide with zinc sulphide (xCdS.yZnS), reaction mass of cadmium sulphide with mercury sulphide (xCdS.yHgS), and those specified elsewhere in this Annex		Acute Tox. 4 * Acute Tox. 4 * Acute Tox. 4 * Aquatic Acute 1 Aquatic Chronic 1	H332 H312 H302 H400 H410
028-043-00-0	cobalt nickel gray periclase; C.I. Pigment Black 25; C.I. 77332; [1] cobalt nickel dioxide; [2] cobalt nickel oxide [3]	68186-89-0 [1] 58591-45-0 [2] 12737-30-3 [3]	Carc. 1A STOT RE 1 Skin Sens. 1	H350i H372** H317
028-052-00-X	nickel barium titanium primrose priderite; C.I. Pigment Yellow 157; C.I. 77900	68610-24-2	Carc. 1A STOT RE 1 Skin Sens. 1	H350i H372** H317

* Minimum classification (see the CLP Regulation for more details).

** The exact exposure route not known (see the CLP Regulation for more details).

3.5 Applications with intentional use of nanosized pigments

As described in section 2.2, pigments for various applications are manufactured from primary pigments with a median size below 100 nm which renders the pigment a nanomaterial, according to the EU nanomaterial definition. For most applications, the pigments form larger particles by aggregation and agglomeration and the dispersed particles, e.g. in a paint, may have particles with a median size well above the 100 nm.

The description of these applications serves as background information for the description of pigments in consumer products marketed in Denmark found in chapter 0.

For some applications, the pigments are disaggregated into smaller particles and the dispersed particles have a particle size distribution closer to the particle size distribution of the primary particles. These fine-dispersed pigments are sometimes referred to as "nanopigments" or "ultrafine pigments". The term "nanopigments" are, however, used for different types of pigments with a particle size distribution with a median particle size below 100 nm:

- Ultrafine grade of pigments (further described in section 3.5.1)
  - 1) Manufactured by comminution (e.g. grinding) of larger particles
  - 2) Manufactured by stopping the crystallization at a certain size
- Nanomica-based pigments – nanomica flakes coated with a pigment (further described in section xxx)
- Nanoclay particles coloured by a dye (further described in section xxx).

The market volume of pigments manufactured as ultrafine grades is not known, but industry contacts have indicated that it most probably is a few percentage points of the total market of pigments.

3.5.1 Transparent coatings

Transparent coatings are used for various applications where the structures and colours of the underlying material should appear through the coating. Applications are e.g. transparent wood paints or coatings with a glazing effect.
Examples of ultra-fine pigments for transparent coatings are Clariant's Hostafine® product range, Sun Chemical's performance pigments for coatings (Sun Chemical, year not indicated), Nano Organic Pigment Dispersion and Nano Transparent Iron Oxide Pigment Disperion from Jetcolour (2014).

One example is Clariant's Hostafine® product range (Clariant, 2014b). The products are marketed for:

- Coloration of wood, e.g. furniture, flooring, joinery and toys
- Transparent wood stains – water-based and water/alcohol combinations
- Tinted sealers and topcoats
- Water-based UV-curable coatings
- Colorants for wood impregnation.

The median particle size (d_{50} in the volumetric particle size distribution) of the pigments is in the range of 57-92 nm. The pigments are indicated as "ultra-finely dispersed pigment dispersions" with high "High color strength & brilliance and outstanding transparency".

TABLE 9
EXAMPLE: PIGMENTS IN THE "HOSTAFINE"® PRODUCT RANGE (BASED ON CLARIANT, 2014B)

Product	CAS No *	Colour Index, C.I.	C.I. No.	Particle size distribution, d_{50}, nm
Hostafine Yellow GR	5102-83-0	Pigment Yellow 13	21100	89
Hostafine Yellow HR	5567-15-7	Pigment Yellow 83	21108	57
Hostafine Red HF3S	61847-48-1	Pigment Red 188	12467	92
Hostafine Red FGR	6535-46-2	Pigment Red 112	12370	90
Hostafine Red F5RK VP 3204	2786-76-7	Pigment Red 170	12475	84
Hostafine Red P2GL	5521-31-3	Pigment Red 179	71130	70
Hostafine Rubine F6B	99402-80-9	Pigment Red 184	12487	73
Hostafine Magenta E VP 2609	980-26-7	Pigment Red 122	73915	68
Hostafine Violet RL VP 2475	6358-30-1	Pigment Violet 23	51319	64
Hostafine Blue B2G	147-14-8	Pigment Blue 15:3	74160	73
Hostafine Green GN	14832-14-5	Pigment Green 7	74260	62
Hostafine Black T 30 VP 2813	1328-53-6	Pigment Black 7	77266	57
Hostafine Black TS 30 VP 3035	1328-53-6	Pigment Black 7	77266	57

* The CAS numbers are derived from the Colour Index numbers indicated in the brochure

Another example is Sun Chemical's performance pigments for coatings (Sun Chemical, year not indicated). Most of the pigments indicated as "transparent" have a surface area above 60 m^2/cm^3 (calculated by multiplying the indicated specific gravity and the surface area in m^2/g) and the surface area of the pigments indicated as "transparent" generally have significantly higher surface areas than other pigments (relationship between pigment size and surface area is discussed later). The transparent products are, in particular, indicated as used for coatings for automotive applications, but also for building/decorative and general industrial applications.

Transparent iron oxide pigments - Many manufacturers provide transparent iron oxide pigments with a size distribution in the nanoscale. As an example, Dyrox Chemicals Company Ltd. (2014) markets transparent iron oxides for automotive paints, wood coatings, plastics applications, industry coatings, printing ink, art coating, cosmetics and powder coating.

3.5.2 Inks

Nanosized pigments are used in various applications in the printing industry where transparency and high colour strength is desired. In any case, the pigments used in inks are relatively small, but many manufacturers market pigment grades specifically indicated to be in the nano-range. Many of these pigment grades are in particular used for ink-jet applications.

Examples are the Microlith® pigment preparations from BASF (2011b), Hostajet PT grades from Clariant (2006), Solvent Based Nano Pigment Dispersion from Jetcolour (2014), Cylcojet inkjet dispersions from Lever Colors (2014), SOCAL® & WINNOFIL® in Offset Inks from Solway or nanopigment preparations from Resun Colour (2014).

The Microlith® pigment preparations from BASF (2011a, 2011b) are described here as one example. The description of the pigment preparations indicates that the small particle size and extremely narrow particle size distribution are obtained by a specialised high-shear kneading technology. The small particle size and narrow particle size distribution affords maximum colour strength and transparency as well as good dispersion stability, according to the manufacturer. The Microlith pigments are marketed in five product ranges used for a variety of applications (BASF, 2014):

- Microlith® A pigment preparations are used in applications such as glossy and transparent decorations on clear films, aluminium and metalized films as well as heat-seal-resistant prints on various packaging materials.
- Microlith® J a series of a new range of high-performance pigment preparations developed for solvent-based and UV inkjet inks.
- Microlith® KJ preparations are specific grades for inkjet.
- Microlith® K pigment preparations are compatible with acrylic, PUR, vinyl and UV-curing ink systems for processes such as rotogravure, screen and wide-format inkjet.
- Microlith® WA pigment preparations are used in applications such as water-based printing inks for PVC floor and wall coverings, as well as for most kinds of packaging materials.

As an example, data for the 19 pigments available in the Mikrolith K® product range are shown in the table below. The median particle sizes of the pigments is the in the range of 39-100 nm (probably the volumetric particle size distribution) as shown in the table below. The pigments are used for solvent-based ink-jet inks for indoor and outdoor graphics.

Many of the pigments are also available in other pigment systems for ink jet inks from BASF where the median size of the dispersed pigments is higher (whereas the median size of the primary particles may possibly be the same as discussed elsewhere).

TABLE 10
EXAMPLE: PIGMENTS IN THE MIKROLITH K® PRODUCT RANGE (BASED ON BASF, 2011B)

Product	CAS No**	Colour Index, C.I.	Particle size, nm *
Yellow 1550 K	5567-15-7	Pigment Yellow 83	not indicated
Yellow 1040 K	5580-57-4	Pigment Yellow 93	not indicated
Yellow 2040 K	106276-80-6	Pigment Yellow 110	50
Yellow 1061 K	31837-42-0	Pigment Yellow 151	100

Brown 3001 K	35869-64-8	Pigment Brown 23	not indicated
Scarlet 3430 K	3905-19-9	Pigment Red 166	not indicated
Red 3890 K	5280-78-4	Pigment Red 144	not indicated
Red 3630 K	84632-65-5	Pigment Red 254	49
Red 4410 K	51920-12-8	Pigment Red 185	not indicated
Magenta 4535 K	3089-17-6	Pigment Red 202	61
Magenta 4330 K	mix	mix	54
Black 0066 K	1328-53-6	Pigment Black 7	not indicated
Blue 7080 K	147-14-8	Pigment Blue 15:3	39
Blue 6480 K	81-77-6	Pigment Blue 60	not indicated
Violet 5700 K		Pigment Violet 37	not indicated
Green 8750 K	14832-14-5	Pigment Green 7	not indicated
White 0022 K	13463-67-7	Pigment White 6	not indicated

* As measured by a disc centrifuging method

** The CAS numbers are derived from the Colour Index numbers indicated in the brochure

Nanographic printing ™ - A new printing technology, Nanographic Printing™ technology differs from other printing technologies according to the inventors because it uses systems and printing processes that employ Landa NanoInk™, a proprietary water-based ink with nano-pigment particles that measure tens of nanometres in size (Landa, 2012). Whereas inkjet printing jets transfer the image directly onto the substrate, Nanography™ first ejects the Landa NanoInk dispersions onto a unique heated blanket, and only then is the ink transferred from the blanket to the substrate in the form of an ultra-thin film. Eight colours are available (Landa, 2012).

Nanosized pigments in conventional inks - Nanoscale pigments may also be applied in conventional inks and paints. Besides the nanoscale grades for ink-jet printing manufactured by Lever Colors, the company indicates that the most cost effective way to add colour strength in gravure and flexographic printing inks is to add up to 5% of nano grade pigment dispersions, which has the added advantage of increasing the tinting strength, colour saturation and gloss beyond what most conventional dispersions do (Lever Colors, 2014).

3.5.3 Transparent plastics e.g. transparent films

3.5.4 Textiles

Pigments are mainly used for textile printing but also some types of dyeing.

Digital textile printing - Textile digital inkjet printing technology is a new printing technology combining information, computer image processing and new materials, and is an extension of the office inkjet printing technology in the area of textiles. The inkjet printing for textiles, like other inkjet printing technologies, applies inks with ultrafine pigments such as the pigments described for inks in section 3.5.2. Printers for textile inkjet printing are currently provided by the major manufactures of inkjet printers. Some of the technologies are marketed as nanotechnologies (e.g. Xennia, 2010).

Viscose dope dying - The Hostafine® pigments described above in section 3.5.2 are also marketed for viscose dope dyeing. Viscose is based on natural cellulose and is used for different textile and non-woven applications. It is pressed through spinnerets and is coagulated in a bath of sulfuric acid. Dope dyeing means that the colorants are added to the viscose before the spinning process takes place (Clariant, 2014).

3.5.5 Other applications of ultra-fine pigments

Ultrafine TiO2 for metallic effect paints

According to the manufacturer, Sachtleben, the UV-TITAN provides a range of micronized transparent titanium dioxide which scatters light when used in combination with metallic pigments, creating differing golden flashes with bluish shifts in hue, a phenomenon known as the Flip-Flop effect. The surface area of the TiO2 is indicated at approximately 60 m^2/g (Sachtleben, 2014).

LCD pigments

An LCD screen is in made up of little cells known as pixels. Each cell contains blue, red and green pigments, which act as filters: the energy passing through them combines with them to create the different colours. These pigments need to be ultra-pure, very fine, resistant and able to spread evenly over the screen surface (Solvay, 2014). The size of the pigments is typically in the 25-40 nm range.

Nanomica pigments

Pigments in the nanosize may also be manufactured as coated nanosized particles. An example of the latter is nanoparticles of mica (phyllosilicate) coated with various organic and inorganic pigments to create pearlescent and iridescent effects that mimic the natural look of stone and rock formations (Torginol, 2004). When the metallic particles are mixed with epoxy, they give the coating a shine that reflects light and creates and eye-catching dramatic colour.

Nanoclay particles coloured by a dye

"Nanopigments" manufactured from nanoclay particles coloured by a dye is an emerging technology and commercial products on the market still seem to be very limited. The coloured nanoclay particles are pigment since the colorant is not dissolved in the medium, but is attached to the surface of nanoclay particles which are dispersed in the medium. An example is Planocolor© Nanopigments, developed by the Dutch TNO Science and Industry (TNO, 2014). By the attachment of a wide range of commercial organic dyes to clay surfaces, various coloured "nanopigments" can be manufactured and the pigments can be dispersed in virtually all polymeric materials and solvent coating systems (TNO, 2014).

The Danish Statutory Nanoproduct Register Order (BEK No 644 of 13 June 2014) does not distinguish between "classical" pigments and these nanoclay-based pigments. In the context of the register, it makes sense to consider these types of colorants as any other class of pigments, as they are present in the final products in particle form and are mainly used to colour the materials.

4. Pigments in consumer products marketed in Denmark

4.1 Selection of applications for the assessment

This part of the survey mainly focuses on pigment-containing mixtures and articles exempt from the Danish Nanoproduct Register for which there is a potential for releases of the free pigments during normal and foreseeable use.

4.1.1 Application exempt from the Nanoproduct Register

As mentioned before, certain product groups were exempt from the required reporting to the Danish Nanoproduct Register. Exemptions relevant for this survey are:

- **Paint**, **wood preservative**, **glue** and **filler** that contain pigment on the nanoscale where the pigment is added solely for the purpose of colouring the mixture.
- Articles of **rubber**, or rubber parts of articles, that contain the nanomaterials carbon black or silicon dioxide.
- Articles or their labels on which the nanomaterial are used directly as **ink**, including newspapers, periodicals, magazines, and packaging that are not coloured in the mass or dyed, etc.
- **Textiles** where nanomaterial is used as ink or for dyeing of the textiles.

A registration of such products can be triggered by other raw materials than pigment, if those raw materials fall under the nano definition.

It should be noted that not all applications of pigments in consumer products are exempt from notification with the Danish Nanoproductregister. This e.g. pertains to the following products *if free nanosized pigments are released during normal or foreseeable use*:

- Printing inks (e.g. cartridges for inkjet printers or laser printers used by consumers).
- Inks for fountain pens and various types of pens such as ballpoint pens, felt tips, marker-pens, etc.
- Cleaning agents (e.g. pigmented soft soap for pigmenting of floors).
- Printing inks for textile printing and textile colourants for home use.
- Modelling wax, "slimy" toys and similar products for children.
- Candles (if nanosized pigments are released as such during use)
- Shoe care products and other products for colouring leather.
- Coloured paper and cardboard.
- Pigments and pigment preparations for colouration of construction materials and coloured mortar.

If the pigments in the listed applications consist of primary particles meeting the EU nanoparticle definition and if these are released as free during use, and if the involved products are sold for private use, the products shall be notified to the Nanoproduct Register.

This survey focuses on applications exempt from notification.

4.1.2 Sources of releases

This survey focuses on products where free nanoparticles (free nanosizes pigments) may be released during normal and foreseeable consumer use.

As concluded in section 2.5, the majority of pigments may potentially have size distributions of the primary/constituents particles rendering the pigments as nanoparticles, according to the EU nanoparticle definition. The actual median size of the aggregated and agglomerated pigment particles is higher in most products and the released particles may similarly have median sizes above 100 nm (although they are still considered nanomaterials according to the EU definition).

Before human or environmental exposure to a substance in an article can take place, the substance must be able to migrate out of, or be liberated from, the article. The guideline for the Danish Nanoproduct Register (Sørensen *et al.*, 2014) considers that free nanoparticles are not released if the nanoparticle is embedded in a matrix:

"However, if the product can only release the nanomaterials with part of the matrix (for example, with a carrying material, so that the nanomaterials are bound in another material), ...then this is not considered a release of the originally added nanomaterial..... For example, this applies to varnished surfaces (both with and without added nanomaterials) where sanding of the varnish results in sanding dust".

In general it is considered that nanomaterials in cured polymers are not released as free nanomaterials. The examples in the guideline for the Nanoproduct Register can be generalised to nanosized pigments in cured plastics, rubbers, coatings (paint, lacquers, varnishes), adhesives, filling materials and sealants.

It is less clear if the examples in the guideline can be generalised to cured inks, e.g. used for paper or textile printing, and this will be further discussed in the following sections.

In general, releases and consumer exposure to the nanosized pigment particles may take place by applications of mixtures containing the pigments i.e. by application of paints, inks, adhesives, etc. before the polymers are cured. This is also noted on page 23 of the guideline for the Nanoproduct Register.

Release of free nanomaterials during normal or foreseeable uses by the consumer is within the scope of the notification requirements for the Danish Nanoproduct Register, whereas release only occurring during the handling of waste or waste water would not trigger notification obligations.

4.1.3 Selected applications

On the basis of the considerations above, the following exempt applications with the potential for releases of free nanosized pigments have been selected for further assessment:

- Paint, lacquers and varnishes
- Adhesives, sealants and filling materials
- Articles or their labels on which the nanomaterial is used directly as ink (the direct use of inks is not exempt)
- Textiles.

In addition, rubber parts containing carbon black is a category that has been selected for further assessment because the Statutory Order on the Nanoproduct Register has a specific exemption for this application area, even the pigments most likely are only released embedded in the rubber matrix.

4.2 Data from the Danish Productregister

Data on pigments in mixtures registered in the Danish Product Register were retrieved in August 2014 on the basis of the gross list of 573 pigments (See Section 1.1.3).

The Danish Product Register includes substances and mixtures used occupationally and which are imported or produced in quantities above 100 kg/year and contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance). Only a few of the pigments are subject to harmonised classification as dangerous and most of these are banned in Denmark (e.g. the lead pigments). For the other pigments without a harmonised classification, the registration only occurs if they are constituents of mixtures which are classified and labelled as dangerous due to the presence of other constituents. Solid polymer compounds and masterbatches used in the production of plastics are not covered by the requirements for notification to the Product Register. The data also do not address articles such as textiles. The data consequently do not provide a complete picture of the presence of the pigments in mixtures placed on the Danish market.

As stated above, the amounts registered are for occupational use only. It is considered likely that the pigments used in paints, varnishes, adhesives, etc. for the professional market (e.g. building paints) are the same or similar as the pigments in paints used by consumers. Mixtures used for industrial applications are considered more likely to have a different composition from the mixtures used by consumers, as different technologies are applied.

Consequently, in the following sections, the pigments used for professional applications are used as the best indication of the pigments that may be present in mixtures for consumer applications.

All pigments registered in the Danish Productregister are listed in Appendix 3. The list indicates for each pigment the number of notified products and the number of notifiers, as well as the total registered consumption (mean figures). For pigments where either the number of products or the number of notifiers is below 3, the data on volumes and applications are confidential and therefore not included.

In total 177 substances from the gross list were registered of which 34 were inorganic pigments and 143 were organic pigments.

The total registered consumption was 28,460 t/y in 2013. The consumption is calculated as the registered import/production (of the substance on its own or in mixtures) from which the registered export is subtracted. For some of the substances, e.g. zinc oxide and carbon black, a major part of the consumption may be for non-pigmentary use.

The titanium oxides accounted for 76% of the total while the iron oxides in total accounted for 15%. This is in reasonable accordance with the global and EU figures described in 3.1 and 3.2.

The registered consumption of the 145 organic pigments totalled about 540 t/y, corresponding to approximately 2% of the total consumption. This is also in reasonable accordance with the figures shown in Table 7, where the 119 pigments registered by the organic pigments consortia represent 2% of the total tonnage registered under REACH.

The information for 82 of the pigments is confidential. The total consumption of these pigments is 104 tonnes, corresponding to 0.4% of the total.

The 15 organic and 15 inorganic pigments with the highest registered consumption are shown in Table 11. These 30 pigments account for 99% of the total consumption registered in the Danish Productregister. The tonnage registered under REACH is indicated in the table as well. The pigments registered with the highest consumption in the Danish Productregister are, in general, also those registered with highest tonnage under REACH. The registered consumption of carbon black is relatively small, reflecting that the consumption of carbon black for non-pigmentary use for manufacture of rubber in Denmark is also small (e.g. no tyre production occurs in Denmark).

One of the 30 pigments is not registered under REACH (CAS No 101357-30-6), but the same substance is registered under another CAS number (pre-registered with the same EC number).

In the production and import/export statistics from Eurostat or Statistics Denmark, volume data on production of pigments in Demark as well as import/export data are confidential and can therefore not be reproduced here.

TABLE 11

THE ORGANIC AND INORGANIC PIGMENTS WITH THE HIGHEST REGISTERED CONSUMPTION IN THE DANISH PRODUCTREGISTER.

CAS No	EC No	Name *1	n, *3 prod-ucts	n, *3 compa-nies	Consump-tion, t/y (mean value) *2	REACH registered tonnage, t/y
Inorganic pigments						
13463-67-7	236-675-5	Titanium dioxide	2,691	256	21,405	1,000,000-10,000,000
1309-37-1	215-168-2	Diiron trioxide	996	145	4,056	100,000 - 1,000,000
1314-13-2	215-222-5	Zinc oxide	563	111	709	100,000 - 1,000,000
1317-80-2	215-282-2	Rutile (TiO2)	119	48	300	10,000 - 100,000
1333-86-4	215-609-9	Carbon black	1,448	190	251	1,100,000 - 11,000,000
1317-61-9	215-277-5	Triiron tetraoxide	341	90	240	100,000 - 1,000,000
51274-00-1	257-098-5	iron hydroxide oxide yellow	472	72	228	100,000 - 1,000,000
1308-38-9	215-160-9	Chromium (III) oxide	105	37	183	10,000 - 100,000
1317-36-8	215-267-0	Lead monoxide	45	12	142	100,000 - 1,000,000
57455-37-5	309-928-3	Silicic acid, aluminium sodium salt, sulfurized	35	17	119	10,000 - 100,000
1317-60-8	215-275-4	Hematite (Fe2O3)	64	14	47	10,000 - 100,000
8007-18-9	232-353-3	Antimony nickel titanium oxide yellow	23	13	36	1,000 - 10,000
101357-30-6	309-928-3 (same as above)	Silicic acid, aluminium sodium salt, sulfurized	6	6	21	not registered
12656-85-8	235-759-9	Lead chromate molybdate sulfate red	33	16	17	1,000 - 10,000
68186-90-3	269-052-1	Chrome antimony titanium buff rutile	63	20	11	10,000 - 100,000
Organic pigments						
147-14-8	205-685-1	C.I. Pigment Blue 15	516	102	57	10,000 - 100,000
1328-53-6	215-524-7	C.I. Pigment Green 7	281	72	44	1,000 - 10,000
3520-72-7	222-530-3	C.I. Pigment Orange 13	8	7	36	100 - 1,000
6358-30-1	613-252-7	C.I. Pigment Violet 023	251	49	36	1,000 - 10,000
6358-31-2	228-768-4	C.I. Pigment Yellow 74	168	43	30	1,000 - 10,000
15793-73-4	239-898-6	C.I. Pigment Orange 34	76	25	22	100 - 1,000
5567-15-7	226-939-8	C.I. Pigment Yellow 83	125	27	20	1,000 - 10,000
36888-99-0	253-256-2	Pigment Yellow 139	65	21	20	1,000-10,000
5281-04-9	226-109-5	C.I. Pigment Red 57:1	21	6	19	10,000 - 100,000
2786-76-7	220-509-3	C.I. Pigment Red 170	144	36	19	100 - 1,000
6535-46-2	229-440-3	C.I. Pigment Red 112	85	26	19	1,000 - 10,000
12236-62-3	235-462-4	C.I. Pigment Orange 36	102	24	18	100 - 1,000
84632-65-5	617-603-5	C.I. Pigment Red 254	84	26	18	10-100
980-26-7	213-561-3	C.I. Pigment Red 122	98	30	17	1,000 - 10,000
1047-16-1	213-879-2	C.I. Pigment Violet 19	153	39	15	1,000 - 10,000

.. Data are confidential

*1 For inorganic pigments the preregistering name is indicated, because the name indicated the composition of the pigment. For organic pigments, the name registered in the Productregister is indicated because the C.I. pigment names are the names usually used to identify the pigments.

*2 Registered consumption = registered manufacture/import - export (average figures).

*3 Number of registered products and number of companies, which have notified products with the pigment.

The table below shows the number of different pigments (CAS numbers), total pigment consumption, and total product volume by main use categories. The categories are the "UC62" use categories applied by the Product Registries by the Nordic Countries (for more details see SPIN (2014)). The total of 14,172 t/y in 2013 is significantly less than the 28,460 t/y indicated above. The data are not retrieved the same day from the Productregister, and the difference is due to some discrepancies in the registering of the titanium dioxide for "other" applications.

The applications are divided into formulation processes, process regulations and end-uses of mixtures. For colouring agents and intermediates, the average concentration is approximately 50 percent. Some of the colouring agents and intermediates may be used in the manufacture of construction materials (concrete, plaster, etc.) and the part used for this application may be considered an end use rather than a formulation process.

For the final products, the concentration is typically in the 1-10% range; this aspect is further discussed in the following sections.

The major application areas are colouring agents and intermediates used in formulation processes and the end-uses of paints, inks, lacquers and varnishes, fillers (incl. sealants), construction materials, reprographic agents (inks), and surface treatment (various products).

The registered pigments for paints, adhesives, lacquers and varnishes, fillers (incl. sealants), adhesives and cleaning agents (incl. maintenance agents) are further described in the following sections with a focus on consumer applications.

TABLE 12
NUMBER OF PIGMENTS AND CONSUMPTION BY MAIN USE CATEGORIES (UC62 CATEGORIES)

	Number of different CAS numbers	Number of products	Number of companies	Consumption of pigment*1, t/y (mean value)	Consumption of products, t/y (mean value)	Percentage (mean value)
Mixtures primarily used for formulation processes and process regulators						
Colouring agents	66	213	39	3,646	7,451	49%
Intermediates	5	15	6	4,727	9,043	52%
Process regulators	11	72	20	21	492	4%
Surface-active agents	19	48	7	2	227	1%
Mixtures primarily for end-uses						
Adhesives, binding agents	34	270	84	61	5,529	1%
Anti-set-off and anti-adhesive agents	17	13	6	0	96	0%
Cleaning/washing agents	10	120	30	13	2,561	0%
Construction materials	35	242	53	939	82,750	1%
Corrosion inhibitors	21	76	22	4	143	3%
Electroplating agents	2	4	3	0	6	5%
Fillers	47	496	103	348	26,555	1%
Impregnation materials	11	13	11	10	645	2%
Insulating materials	7	13	10	0	25	1%
Lubricants and additives	7	55	19	1	25	3%
Non-agricultural pesticides and preservatives	17	178	30	-279	3,609	-
Reprographic agents	107	178	34	581	3,602	16%
Welding and soldering agents	5	13	5	137	1,798	8%
Cutting fluids	3	6	4	1	10	6%
Paints, lacquers and varnishes	126	2,216	131	3,806	56,073	7%
Surface treatment	37	141	55	107	1,609	7%
Other						
Others (indicated as "others")	21	55	29	32	784	4%
Confidential	-	-	-	14	2,606	1%
Grand Total (rounded)	**174**	**4,393**	**355**	**14,172**	**205,641**	**174**

*1 Consumption of pigment = pigment content of consumed mixtures. The consumption of the mixtures is calculated as registered production/import - export.

4.3 Paint, lacquers and varnishes

4.3.1 Market for the products for consumer applications

Production, import and export statistics
The consumption of paints for all applications in Denmark, based on statistics from Eurostat, is shown in Table 13. The dataset is extracted from the Eurostat database combining production, import and export by the PRODCOM (production statistics) nomenclature. The use of data on import/export by combined nomenclature (CN) codes extracted from the database of Statistics Denmark results in slightly different figures. According to the database of Statistics Denmark, the total import in 2013 was 43,000 tonnes and the export was 48,000 tonnes.

The consumption in Denmark is of the same magnitude as production, import and export, indicating that a major part of the paint produced in Denmark is exported. The major manufacturers of paints in Denmark are companies with manufacturing facilities in many countries (e.g. other Nordic countries) and it is typical that the different facilities focus on specific product categories, and there is an extensive inter-company exchange of products by import/export.

Water-based paints based on acrylic or vinyl polymers account for the majority of the paints. The paints used by consumers, e.g. for wall-paints and wood/metal, would mainly fall within this category.

Pigment content - The concentration of pigments in the paints varies considerably. The average concentration of pigments registered in the Productregister for all applications in 2013 was 7% which is surprisingly low (Table 12). White water-based paints account for a significant part of the total paint consumption. The concentration of titanium dioxide in the white water-based paints is typically reported to be 20% (Poulsen *et al.*, 2002). The pigment concentration seems to be in the same range for both organic and inorganic pigments. If the average pigment content is assumed to be in the 10-15% range, the total pigment content of the 60,000 t/y paint consumed in Denmark would be in the range of 6,000-9,000 t/y. The total quantity registered in the Productregister in 2013 was 3,806 tonnes, as shown in Table 12.

TABLE 13
PRODUCTION, IMPORT AND EXPORT OF PAINTS BY PRODCOM CATEGORY, DENMARK 2013 (EUROSTAT, 2014) *1

PRODCOM code		Tonnage, 2013, t/y			
		Production	Import	Export	Consumption *
20301150	Paints and varnishes, based on acrylic or vinyl polymers dispersed or dissolved in an aqueous medium (including enamels and lacquers)	46,427	28,083	35,543	38,967
20301170	Other paints, varnishes dispersed or dissolved in an aqueous medium	4,942	3,975	7,062	1,855
20301225	Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium, weight of the solvent >50% of the weight of the solution including enamels and lacquers	0	1,909	323	1,586
20301229	Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium including enamels and lacquers excluding weight of the solvent >50% of the weight of the solution	324	3,673	2,804	1,193
20301230	Paints and varnishes, based on acrylic or vinyl polymers dispersed/dissolved in non-aqueous medium, weight of the solvent >50% of the solution weight including enamels and lacquers	35	561	218	378
20301250	Other paints and varnishes based on acrylic or vinyl polymers	2,957	3,292	1,124	5,126
20301270	Paints and varnishes: solutions n.e.c.	226	506	372	361
20301290	Other paints and varnishes based on synthetic polymers n.e.c.	2,835	11,657	4,227	10,265
	Total	**57,747**	**53,656**	**51,672**	**59,731**

*1 Consumption in Denmark = production + import - export

Paints used by consumers
As indicated above, the total consumption of paints and varnishes in Denmark in 2013 was approximately 60,000 tonnes. In the statistics, it is not indicated how much of this was used by consumers. The total quantity of paint (incl. wood preservatives) registered in the Productregister was 56,000 (38,000-75,000) tonnes, indicating that the majority of the quantity of the water-based paints are registered even if they do not contain substances with a harmonised classification.

The Danish Coatings and Adhesives Association (DFL) keeps some statistics on the market for building paints, but it does not indicate how much of the building paints are used by consumers. For this survey DFL has undertaken a consultation of key actors in the market. According to the statistics by DFL, the market for building paint (decorative paint = indoor and outdoor paints for walls, ceilings, woodwork, concrete and metal on buildings) in Denmark in 2013 totalled approximately 30.5 million litres. It is estimated by market actors that consumer applications (DIY market) account for approximately 48%, corresponding to 14.6 million litres. The typical density of building paint is in the range of 1.2-1.4 with solvent-based alkyd paints on the low end and water-based wall paints on the high end (Poulsen *et al.*, 2002). If an average density of 1.3-1.4 is used and some uncertainty is added to the estimates on total volumes, the total consumption of building paints by consumers in 2013 can be estimated at 16,000-21,000 tonnes. In addition to this, consumers use a small amount of other paints e.g. for painting leisure boats and cars. It is estimated that the consumption for other applications will be small as compared to building paints.

4.3.2 Pigments in the products

Data from the Danish Productregister

Data from the Danish Productregister on pigments used in paint for non-industrial applications are shown in Appendix 3. The table thus excludes application areas (UC62 categories) where it is explicitly indicated that the paint and varnishes are for industrial applications.

In total, 112 different pigments are registered for the relevant applications. For 66 of these, the data are confidential.

TABLE 14
PIGMENTS IN PAINT AND VARNISHES EXCL. INDUSTRIAL APPLICATIONS IN THE DANISH PRODUCTREGISTER

Product category according to UCn Codes	Consumption *1 TiO_2, t/y	Consumption other pigments, t/y	Total	Number of registered pigments
Paint organic solvent-based, non-industrial	33	18	53	40
Paint water-based, non-industrial	245	162	407	28
Anti-rust paint	56	20	76	46
Other paints *2	824	564	1,388	108
Total non-industrial	1,158	764	1,922	112

*1 Registered consumption = content of registered products. Consumption = production/import - export

*2 Include UCn code B15720, M05413, M05433, MO5441, MO5442, MO5443, MO5444, M05996, M05998, M05999. The majority is included in UC62 code M05999 "other paints and varnishes". The group likely includes both water-based and solvent-based paints and varnishes, and is likely used when the exact application of the paints are not known by the importer.

The 13 pigments with the highest registered consumption within each of four groups of paint and varnishes are shown in Table 15. (For some of the groups more than 13 pigments are shown in order to complete the table). For each of the groups, the pigments listed in Table 15 represent more than 88% of the total use of pigments.

The table excludes application areas (UC62 categories) where it is explicitly indicated that the paint and varnishes are for industrial applications or are powder lacquers (assumed to be for industrial applications). The paints and varnishes are divided into the following groups: Water-based paint and varnishes, solvent-based, paint and varnishes for rust protection and a group of other paints and varnishes. The latter group includes various product categories and a significant part of this may actually be for industrial applications.

The data in the Productregister are registered as ranges with minimum and maximum values. As an example, for the total registered consumption of the water-based paints, the average in 2013 was 407 tonnes. A simple addition of all minimum and maximum values (combinations of CAS No and UC62 codes) results in a range of 172-641 tonnes. If arithmetic methods for addition of uncertainty distributions (uncertainty of the result is represented by the square root of the sum of the squares) is applied, the resulting range would be 328-485 tonnes.

Whereas the total quantities should be interpreted with caution, it is considered that the relative contribution of the different pigments for water-based and solvent-based paints gives a dependable indication of the pigments used in paints marketed in Denmark for professional use. Whereas the pigments in paints for industrial applications may be different from the pigment in paints for consumers, it is considered that the pigments in paints used by professionals (mainly building paints) are likely similar to the pigments used in paints for consumers. This has been confirmed by DFL, which does not have any information indicting any major differences.

The building paints that may be used by consumers are usually contained within the water-based and solvent-based paint and varnishes groups. It is more or less the same pigments used in the two groups of paints, whereas in "other paints" some of the pigments differ.

Titanium dioxide and diiron dioxide are the main pigments within all groups.

TABLE 15
PIGMENTS WITH THE HIGHEST REGISTERED CONSUMPTION IN PAINT AND VARNISHES FOR NON-INDUSTRIAL APPLICATIONS IN THE DANISH PRODUCT

CAS No	Chemical name	Registered consumption, average t/y *2				
		Water-based	Solvent-based	Rust protection	Other paints 2*	Total
13463-67-7	Titanium dioxide	243.8	33.3	54.2	823.8	1,155
1309-37-1	Diiron trioxide	50.8	5.8	10.4	150.8	218
1317-61-9	Triiron tetraoxide	43.2	0.4	0.7	39.9	84
147-14-8	C.I. Pigment Blue 15	3.6	0.3	0.6	10.2	15
14302-13-7	C.I. Pigment Green 36	3.3	..	0.4	4.5	8
6358-31-2	C.I. Pigment Yellow 74	2.3	1.0	..	4.9	8
1328-53-6	C.I. Pigment Green 7	2.2	0.2	..	8.9	11
1314-13-2	Zinc oxide	2.1	2.4	1.2	38.4	44
51274-00-1	Iron hydroxide oxide yellow	2.0	0.3	0.6	32.8	36
6535-46-2	C.I. Pigment Red 112	1.8	0.7	0.2	5.0	8
1317-80-2	Rutile (TiO2)	1.3	..	..	17.1	18
1333-86-4	Carbon black	1.2	3.4	1.9	66.4	73
1308-38-9	Chromium (III) oxide	0.0	..	..	57.7	58
1047-16-1	C.I. Pigment Violet 19	..	0.1	..	7.5	8
4378-61-4	C.I. Pigment Red 168	..	0.1	..	2.2	2
5567-15-7	C.I. Pigment Yellow 83	..	0.2	0.2	5.6	6
6358-30-1	C.I. Pigment Violet 023	..	0.1	..	4.7	5
2786-76-7	C.I. Pigment Red 170	..	..	0.6	3.7	4
1328-53-6	C.I. Pigment Green 7	..	..	0.0	8.9	9
12236-62-3	C.I. Pigment Orange 36	..	..	0.2	6.5	7
3520-72-7	C.I. Pigment Orange 13	..	..	..	36.0	36
Total listed above		358	48	71	1,299	1,777
Total incl. other and confidential		407	52	76	1,388	1,923

*1 Registered consumption = content of registered products. Consumption = production/import - export

*2 Includes UC62 code B15720, M05413, M05433, MO5441, MO5442, MO5443, MO5444, M05996, M05998, M05999. The majority is included in UC62 code M05999 "other paints and varnishes". The group likely includes both water-based and solvent-based paints and varnishes, and is likely used when the exact application of the paints are not known by the importer.

.. Volumes are confidential or the substance is not used.

Applications where ultrafine pigments are used for colouration

As described in section 3.5.1, ultrafine pigments are used in some types of transparent coatings (e.g. for wood colouration) and transparent wood preservatives. These groups are included in the group paint, varnishes, etc. in the Danish Productregister. In these products, the pigments in the suspension (primary particles, aggregates and agglomerates) generally have a volumetric particle size distribution with a median diameter < 100 nm.

No data are available to indicate how much of the total consumption these applications account for in Denmark or whether specific pigments are used for these applications. From the technical information from the manufacturers of ultrafine pigments, it appears that, in general, the ultrafine pigments are the same as the pigments used in other paints (and likely, the size distribution of the primary particles is the same).

The exposure pathways and emission factors for these products are not considered to be different from the pathways and emission factors for paints in general.

It should be noted that paints where pigments are added that are not solely for the purpose of providing colour are not exempt from registration. However, within the scope of this project, no distinction can be made between pigments added solely with the intention of providing colour and pigments added to also provide other properties.

4.3.3 Potential for consumer and environmental exposure

Potential releases from painted surfaces

As indicated elsewhere, the guidelines to the Danish Nanoproduct Register (Sørensen *et al.*, 2014) state that scientific studies have shown that free nanoparticles added to paint are not released when sanding painted surfaces. Among the scientific evidence are the results of the NANOKEM programme, "Nanoparticles in the paint- and lacquer industry. Exposure and toxic properties", undertaken by the Danish National Research Centre for the Working Environment (NRCWE).

Addition of nanoparticles to paint, lacquer and plaster may change the amount of dust particles generated during sanding of these materials, whereas the particle-size distribution of the sanding dust rarely changes (Kooponen *et al.*, 2011; NRCWE, 2012b). Hence, the results indicate that the type of paint, lacquer or plaster, i.e. the matrix material, is a stronger determinant for the size distribution of sanding dust than the nanoparticles in the materials. The results also demonstrate that the addition of nanoparticles to paint does not increase the adverse effects of dust from paint, lacquer and plaster. The matrix itself (paint, lacquer and plaster) has a greater impact on the adverse effects than the addition of nanoparticles (NRCWE, 2012a).

Similar results have been obtained in German studies. Göhler *et al.* (2011) did not find any significant difference in the formation of nanoparticles during the sanding process between coatings containing and those not containing nanoparticle additives. Vorbau *et al.* (2009) found that the released particle mass depended on substrate and coating, but there was no significant correlation to nanoparticle content. TEM and EDX images showed that the particles <100 nm remain embedded in the coarse wear particles (Vorbau, 2009).

Potential release by application of paint, lacquers and varnishes

Consequently, the assessment of the potential for exposure to free nanosized pigments will focus on the application of the paint, lacquers and varnishes, where the pigments are suspended in the mixtures. The guidance in support of the Danish Nanoproduct Register states (p. 23) that liquid mixtures (including paint, lacquers, and similar products containing nanomaterials) are considered products to which the user can be exposed to the nanomaterials. Thus, these products should be registered, unless exempt due to other criteria.

Poulsen *et al.* (2002) assessed the waste generation (including discharges to waste water) and environmental impact of application of paints by consumers. The study found that the actual waste generation (spillage, remaining paint in the tools, etc.) from paint jobs typically accounted for 8 to 30% of the purchased amount of paint. In most of the waste scenarios, the waste generated was disposed of as follows: Between 65 and 97% of the generated paint waste ended up as solid waste, while 3 to 35% of the total waste ended up in the sewer system. Regarding outdoor paint jobs without any covering material, the spillage to the ground was estimated at approximately 1% of the total consumption of paint. The assessment demonstrated that the releases from consumer's painting were larger than from professional painting, because the professional painters generally apply waste reducing routines.

The Specific Environmental Release Categories (SPERCs) from the European Council of Paint, Printing Ink and Artists 'Colours (CEPE) use different emissions factors for paint used by consumers, professionals and industry (CEPE, 2013). The SPERCs apply the following emission factors for solids in paint applied by consumers: 1% to waste water from all applications and 0.5% to soil for applications outdoors (CEPE, 2013). SPERCs for professional application by spray painting are 2.2% to air, 2% to waste water, and the releases to soil is indicated as "to be advised". Emission factors for consumer use by spray painting are not provided for consumer application, but it may be considered similar to the application by professionals.

Exposure routes

The potential routes for exposure to nanosized pigments in paint, lacquers and varnishes are listed in Table 16.

TABLE 16
POTENTIAL EXPOSURE TO NANOSIZED PIGMENTS IN PAINT, LACQUERS AND VARNISHES BY APPLICATION

Paint, lacquers and varnishes	
Exposure routes for consumer exposure	
Dermal exposure	By application of paints and cleaning of tools, the user will often be exposed to paints on the hands (unless they use gloves). Paints on the hands would shortly after application polymerise and the exposure to the free pigments in the paints would then be considered to be small.
Oral exposure	Oral exposure to free pigments in paint, lacquers and varnishes is considered unlikely.
Inhalation exposure	By spray painting, the user may be exposed to free pigments in aerosols.
Exposure routes for environmental exposure	
Environmental exposure via wastewater	The main route for environmental exposure to free pigments in paint, lacquers and varnishes is considered to be via wastewater. For ***water-based paints***, a part of the paint is released to wastewater by cleaning of brushes and other tools by water. In the paints, the pigments are kept in dispersion by the use of surface active agents. By the dilution of the paint through the washing and discharge to the sewer system, the pigments will likely further aggregate and agglomerate forming larger particles. By the sewage treatment the majority of the pigments will likely end up in the sludge and be disposed of with the sludge (agricultural soil or incineration). A smaller portion may be discharged to surface water with the outlet from the wastewater treatment plants. A portion of the waste water may not be cleaned in sewage treatment plants. In Denmark this portion would represent a few percentages (e.g. overflow by heavy rain) but the percentage may be higher in some other countries. The pigments in this waste water will be discharged directly to surface water. No data on the fate of the pigments by wastewater treatment has been identified. Environment Canada (2013) conservatively estimates, based on expert judgement, carbon black removal efficiency from influent resulting from the wastewater treatment process at 50% where lagoons or primary treatments exist (conservatively in the sense that the removal efficiency likely is higher).

	The brushes and other tools from the use of ***solvent-based paints*** may either be cleaned in a solvent (disposed of as hazardous waste) or in a "brush cleaner" with a subsequent cleaning with water. In the latter case, the paint is discharged to the sewer system in the same way as water-based paints.
Environmental exposure via air	During outdoor application of spray paint, a fraction of the paint may be spread to the surroundings as aerosols. Most likely, the paint in the aerosols will polymerise while either still in the air or shortly after the settling of the aerosols. The release of free pigments to the environment by this route is considered insignificant.
Environmental exposure by other routes	During outdoor application of paint and wood preservatives, a fraction of the paint may be released to soil by spillage. The paint or preservative is likely to polymerise shortly after the spill, but a minor part of the pigments in the spill may be released as free particles to the soil, in particular if the soil has a high moisture content. From outdoor paints, the pigments will be released together with abraded paints and through maintenance of the painted surfaces. As described in the main text above for sanding of painted surfaces, the release of free pigments by these processes is considered insignificant. It cannot be ruled out that a small part of the pigments may be released from the surfaces of paints during use as free particles, but no data on such releases are available.

4.4 Adhesives, sealants, putty and filling materials

4.4.1 Market for the products for consumer applications

Production, import and export statistics
The consumption of adhesives, sealants, putty and filling materials for all applications in Denmark based on statistics from Eurostat is shown in Table 17. The dataset is extracted from the Eurostat database combining production, import and export by the PRODCOM (production statistics) nomenclature. Data on import/export in combined nomenclature (CN) codes extracted from the database of Statistics Denmark show almost identical figures.

The total product tonnage for adhesives and binding agents registered in the Danish Productregister (Table 12) is 5,529 t/y, close to the consumption level estimated on the basis of the statistics.

The total consumption of "fillers" in the Productregister in 2013 is 26,555 tonnes with a total content of 348 tonnes pigments. The consumption according to the statistics of glaziers' putty, painters' fillings, caulking compounds (sealants) and similar products were approximately 13,000 tonnes. The "fillers" (UC62 code) likely cover more product types than covered by the statistics and may also include fillers used as raw materials e.g. in plastics. The total volume is significantly lower for the more narrowly defined "Sealant and filling materials" based on the national UCN codes (

Table 18).

TABLE 17
PRODUCTION, IMPORT AND EXPORT OF ADHESIVES, SEALANTS AND FILLING MATERIAL BY PRODCOM CATEGORY, DENMARK 2013 (EUROSTAT, 2014) *1

PRODCOM code		Tonnage, 2013, t/y			
		Production	Import	Export	Consumption *
20302253	Glaziers' putty, grafting putty, resin cements, caulking compounds and other mastics	5,692	9,486	8,534	6,644
20302255	Painters' fillings	2,896	14,284	10,613	6,569
20521080	Prepared glues and other prepared adhesives, n.e.c.	1,674	12,891	6,454	8,111
	Total	**10,262**	**36,664**	**25,602**	**21,324**

*1 Consumption in Denmark = production + import - export

Products used by consumers
It is not indicated in the statistics how much of the registered consumption of adhesives, sealants, pilling materials, etc. was used by consumers. The total quantity of these products registered in the Productregister was in fact higher than suggested from the statistics, which may indicate that the majority was used for industrial and professional applications.

The Danish Coatings and Adhesives Association (DFL) does not keep statistics on the market for these products as the number of key actors in the market is very low, and the data consequently are considered confidential.

Sealants and putty - The total consumption of sealants and putty in 2013 was approximately 6,600 tonnes according to the statistics. In a survey of consumer products from 2004, the total consumption of joint sealants in Denmark was estimated at 6,000-8,000 t/y (Nilsson *et al.*, 2004). The authors of the survey assumed, in the absence of actual data, that consumption in Denmark was divided equally between private and professional users, i.e. that some 3,000-4,000 t/y was used by consumers.

Adhesives - According to the statistics, the total consumption of adhesives in 2013 was 8,100 t/y while about 5,500 t/y was registered in the Productregister. Some water-based adhesives are likely not registered in the Productregister, and the difference cannot be interpreted to be the volume used by consumers. A survey of adhesives used by consumers for hobby applications did not provide any estimates on the total consumption of adhesives for consumer applications (Nilsson and Jensen, 2003). The majority of the adhesives are most likely used for industrial and professional applications.

Filling materials - The registered use of painters' fillings in 2013 was 6,600 t/y. Filling materials have not been covered by any of the Danish EPA's consumer product surveys. Filling materials are used by consumers for DIY applications, but no data have been identified that may be used to estimate the share of the market for consumer applications.

4.4.2 Pigments in the products
Contrary to the situation for paints and inks, the pigments used for these application areas are nearly 100% inorganic pigments, with titanium dioxide, carbon black and the iron oxides as the main pigments.

Relatively few pigments and in small quantities are used for consumer applications. Titanium dioxide, diiron trioxide and carbon black account for nearly 100% of the total quantity.

The table excludes application areas (UCN categories) where it is explicitly indicated that adhesives are for industrial applications. For sealants, putty and filling materials, no specific UCN codes are applied for industrial applications and the table includes all registered consumption.

For each of the product categories the information is confidential for approximately half of the used pigments, representing less than 8% of the total volume.

Products used by professionals and consumers do not differ significantly as to the colours of products. The pigments listed in the table are likely also the same pigments present in consumer products.

TABLE 18
PIGMENTS WITH NON-CONFIDENTIAL REGISTERED CONSUMPTION IN ADHESIVES, SEALANTS, PUTTY AND FILLING MATERAILS FOR NON-INDUSTRIAL APPLICATIONS IN DANISH PRODUCTS

CAS No	Chemical name	Registered consumption, average t/y *1	
		Sealant, putty and filling materials *2	Adhesives for non-industrial applications *2
13463-67-7	Titanium dioxide	69.7	3.1
1309-37-1	Diiron trioxide	44.6	1.5
1333-86-4	Carbon black	28.8	9.3
51274-00-1	Iron hydroxide oxide yellow	19.0	..
1317-61-9	Triiron tetraoxide	15.7	0.01
1317-80-2	Rutile (TiO2)	11.8	..
1308-38-9	Chromium (III) oxide	6.7	..
57455-37-5	Silicic acid, aluminum sodium salt, sulfurized	5.8	..
68186-94-7	Manganese ferrite black spinel	1.6	..
4378-61-4	C.I. Pigment Red 168	0.3	..
147-14-8	C.I. Pigment Blue 15	0.2	..
1328-53-6	C.I. Pigment Green 7	0.2	..
1314-13-2	Zinc oxide	0.0	0.4
Total listed above		204.4	14.3
Total incl. confidential		222	14.8
Total number of CAS Numbers		39	11

*1 Registered consumption = content of registered products. Consumption = production/import - export
*2 According to UCN Codes.
.. Volumes are confidential or the substance is not used.

4.4.3 Potential for consumer and environmental exposure

Potential release by application of adhesives, sealants and filling materials
Pigments are ascertained mainly to be released from adhesives, sealants and filling materials by the application of the mixtures before the mixtures are polymerised and cured.

SPERC - Emissions of substances other than solvent in adhesives and sealants have been estimated in a SPERC developed by the Association of the European Adhesive & Sealant Industry (FEICA). It is stated that the wide dispersive use of adhesives and sealants results in environmental emissions that are similar to the related wide dispersive use of paints, lacquers and varnishes. For indoor use, the SPERCs apply an emission factor of 1.5% to waste water and no emissions to air and soil; this factor is the same for both consumer and professional applications (FEICA, 2013). The emission to waste water is based on the cleaning of cloth, sponges, brushes and other application tools using water. No distinction between solvent-based and water-based adhesives and sealants is made; hence, the emission to water for the solvent-based products is a worst case estimate.

Outdoor uses of adhesives, sealants and filling materials typically occurs in construction applications, and the emissions from these uses are covered by the SPERCs authorised by European Federation for Construction Chemicals (EFCC) (FEICA, 2013). Because of the similarities in environmental emissions with the wide dispersive use of paints, lacquers and varnishes, the same release fractions are used in the case of adhesives, sealants and filling materials. Thus, the emission factor to waste water is 1% and no emission to air and soil is predicted (EFCC, 2012).

The assessment of exposure to substances in joint sealants undertaken by Nilsson *et al.* (2004) only included inhalation exposure to volatile substances and did not quantify possible releases by other pathways.

Potential releases from cured materials

The guideline for the Danish Nanoproduct Register (Sørensen *et al.*, 2014) states as discussed in section 4.3.3 that scientific studies have shown that free nanoparticles added to paint are not released when sanding painted surfaces. The guideline does not address the possible releases from cured adhesives, sealants, filling materials, etc.

Exposure routes

The potential routes for exposure to nanosized pigments in adhesives, sealants and filling materials are listed in Table 19.

TABLE 19
POTENTIAL EXPOSURE TO NANOSIZED PIGMENTS IN ADHESIVES, SEALANTS AND FILLING MATERIALS BY APPLICATION

Adhesives, sealants and filling materials	
Exposure routes for consumer exposure	
Dermal exposure	During application of adhesives, sealants and filling materials and cleaning of tools, the user can be exposed to the substances via the hands (unless they use gloves). After application, adhesives on the hands would shortly polymerise; the exposure to the free pigments in the paints would then be considered to be small. Dermal exposure takes place both for water-based and solvent-based products.
Oral exposure	Oral exposure to free pigments in adhesives, sealants and filling materials is considered unlikely.
Inhalation exposure	Adhesives have different application techniques, including spraying. In this case, the user may be exposed to free pigments in aerosols. According to the survey of Nilsson and Jensen (2003), all identified adhesive sprays for consumers were solvent-based.
Exposure routes for environmental exposure	
Environmental exposure via wastewater	**Water-based products** The main route for environmental exposure to free pigments in adhesives, sealants and filling material is considered to be via wastewater during cleaning of cloth, sponges and other tools using water. This is relevant only for water-based products.

	It is common during use of water-based adhesives (e.g. for wood) to remove excess adhesive using a cloth or sponge with water, and clean the tools in the sink. According to the survey of consumer products by Nilsson and Jensen (2003), water-based adhesives used for hobby purposes included some textile adhesives, "school glue", glue sticks, wood adhesives (polyvinyl acetate dispersions) and "hobby adhesives", whereas other adhesives such as contact adhesive, two-component adhesive and plastic adhesives were solvent-based. Water-based sealants used by consumers include acrylic joint sealants and water-soluble silicates (Nilsson *et al.*, 2004). As described for paints, the pigments are likely kept in dispersion in the adhesives and sealants by the use of surface active agents. During the dilution of the substances by washing and discharge to the sewer system, the pigments likely will further aggregate and agglomerate forming larger particles. The likely fate of the pigments during sewage treatment is described under paint and varnishes. **Solvent-based products** The cloth, sponges and other tools from the use of solvent-based products may either be cleaned in a solvent (disposed of as hazardous waste) or more likely be disposed of with solid waste. The release to the sewage system from application of solvent-based products is considered insignificant.
Environmental exposure via air	Outdoor uses of adhesives, sealants and filling materials are typically in construction applications. Spray applications are not assumed to be a primary application technique for outdoor use and therefore environmental exposure via air is considered unlikely.
Environmental exposure by other routes	Environmental exposure from by other routes is considered negligible.

4.5 Inks on printed matter

This section covers inks on printed matter, i.e. articles or their labels on which the nanomaterial is used directly as ink, as these applications are exempt from the Nanoproduct Register. Inks used in textiles are included in section 4.6.

Based on the current interpretation, printing inks (e.g. cartridges for inkjet or laser printers used by consumers) and inks for various types of pens used by the consumers are not exempt from the Nanoproduct Register and are therefore outside the scope of this survey.

4.5.1 Market for the products for consumer applications

The majority of printed matter used by consumers is printed in Denmark and the consumption of inks in Denmark may be used as a first indication of the tonnages of inks in printed matter and the type of pigments used.

Inks consist of pigments, resin, oil or carriers and additives. The pigment and resin content of the inks depends on the application. According to USink (2014), a typical black ink for letterpress contains 12-14% carbon black and 0-4% resin, whereas a black ink for web offset typically contains 17-20% and 3-18% resin. A typical colour ink for letterpress contains 7-10% pigment and 5-10% resin, whereas for web offset, it contains 10-15% and 10-25% resin. The major fraction of the inks are oil or carrier (30-85%) while additives takes up a small part (<5%).

The consumption of ink in Denmark in 2013 can be estimated at 10,900 tonnes based on the statistics. The majority of the ink was imported.

The total consumption registered in the Productregister in 2013 was 3,600 tonnes with a pigment content of 581 tonnes (16%). Many water-based inks are likely not catalogued in the Productregister.

If it is assumed that the consumed inks contain 12-20% pigments, the consumption, as based on the statistics, would correspond to approximately 1,200-2,000 tonnes pigments per year.

TABLE 20
PRODUCTION, IMPORT AND EXPORT AF INKS BY PRODCOM CATEGORY, DENMARK 2013 (EUROSTAT, 2014) *1

PRODCOM code		Tonnage, 2013, t/y			
		Production	Import	Export	Consumption *
20302450	Black printing inks	37	1,854	124	1,767
20302470	Printing inks (excluding black)	2,505	8,626	2,036	9,095
	Total	2,542	10,480	2,159	10,862

*1 Consumption in Denmark = production + import - export

Statistics on production, import and export of printed matter in Denmark is not available from Statistics Denmark or Eurostat. Prodcom from Eurostat includes such information for most Member States, but not for Denmark.

The Graphic Association of Denmark (GA) prepares some statistics but not in quantitative terms of printed matter. The total sale from the printing industry in 2013 was approximately 10 billion DKK. The import and export of printed matter balanced each other to some extent, with an import and export of approximately 2.5 billion DKK, respectively, annually (GA, 2014). The data confirm the assumption that the majority of the printed matter distributed to consumers is printed in Denmark. Furthermore, the data indicate that the total content of ink in printed matter put on the Danish market is close to the total consumption of inks for printing in Denmark.

A survey from 2012 estimated the paper and cardboard potential for private households in Denmark in 2010, i.e. the amount of paper and cardboard expected to reach private households (Kaysen, 2012). The different categories of printed matter included in the survey and the estimated potentials are given in Table 21.

The total amount of printed matter expected to reach Danish households is therefore 390,000 tonnes nationally (151.6 kg per private household).

The amount of inks used varies by type of printed matter. In a printed book with few illustrations the ink accounts for approximately 0.1% of the total weight, whereas in a district advertising paper the ink may account for up to 3% of the total (Silfverber et al, 1999).

TABLE 21
PAPER AND CARDBOARD POTENTIAL IN DENMARK IN 2010 (KAYSEN, 2012)

Category	Potential			
	Total	kg per household		
	1,000 [tonnes]	Best estimate	Min	Max
Daily newspapers	65.1	25.3	15.9	57.0
Local free papers	38.3	14.9	2.1	40.9
Weekly and monthly magazines	22.9	8.9	7.9	15.1
Trade and scientific magazines as well as bulletins for members of an organisation	14.3	5.6	5.6	5.6
Distribution of telephone directories	2.5	1.0	0.4	1.7
Unaddressed printed matters	166.5	64.7	36.8	83.4
Addressed mail	33.9	13.2	13.2	13.2
Miscellaneous paper	5.3	2.0	2.0	2.0
Cardboard	41.2	16.0	16.0	16.0
Total	390,0	151.6	110.6	196.3

4.5.2 Pigments in the products

Data from the Danish Productregister on pigments used in reprographic agents (mainly printing inks) are shown in Appendix 4. In total, 108 pigments are registered for this application area; of these, 31 have non-confidential information. The 31 pigments listed in Appendix 4 account for 93% of the total consumption.

The total registered consumption is 464 t/y. The registered consumption is relatively small compared with the pigment content of 1,200-2,000 t/y, estimated on the basis of the statistical data on use of inks in Denmark. It indicates that a significant portion of the water-based inks do not include substances with a harmonised classification and are therefore not notified with the Productregister. The Productregister data are divided on various national UCN codes (solvent-based, water-based, etc.), but data for many of the substances are confidential when represented by the more detailed national codes. The objective in this context is not to estimate potential releases from the printing process, but rather the potential releases from the printed matter, and for this purpose, the overall data on the use in reprographic agents are considered sufficient.

Consumption figures for the 15 pigments with the highest consumption volumes, representing 80% of total consumption, are shown in Table 22.

As mentioned elsewhere, pigments in inks are generally of small size. A dried printing ink film is usually 1–1.5 µm thick; therefore, all of the embedded particles are normally considerably smaller than 1 µm (Henker *et al.*, 2013).

TABLE 22
THE 15 PIGMENTS WITH THE HIGHEST REGISTERED CONSUMPTION IN REPROGRAPHIC AGENTS (MAINLY PRINTING INKS) IN THE DANISH PRODUCTREGISTER

CAS No	Pigment name	Consumption, t/y
13463-67-7	Titanium dioxide	227.0
1333-86-4	Carbon black	28.6
147-14-8	C.I. Pigment Blue 15	26.7
1328-53-6	C.I. Pigment Green 7	23.9
6358-30-1	C.I. Pigment Violet 023	19.6
5281-04-9	C.I. Pigment Red 57:1	19.0
15793-73-4	C.I. Pigment Orange 34	16.4
6358-31-2	C.I. Pigment Yellow 74	10.4
1309-37-1	Diiron trioxide	10.3
5160-02-1	C.I. Pigment Red 53, barium salt (2:1)	9.8
51274-00-1	Iron hydroxide oxide yellow	6.8
980-26-7	C.I. Pigment Red 122	5.5
6041-94-7	C.I. Pigment Red 2	4.3
5102-83-0	C.I. Pigment Yellow 13	3.9
3905-19-9	C.I. Pigment Red 166	2.9
Total listed above		412
Total all pigments (incl. confidential)		464
Total number of CAS Numbers		108

4.5.3 Potential for consumer and environmental exposure

Potential for releases of pigments from the printed matter

Even though most commercial printing inks contain pigment particles in the nanoscale, exposure from printed surfaces is not expected to occur, since the nanoscale object will be completely embedded in a polymer matrix and thus completely covered with binder material. Hence, no exposure to free pigment particles is expected.

This supposition was confirmed in a study commissioned by the German Paint and Printing Ink Association (VdL), who investigated the migration behaviour of nanoscale pigment particles from the printing ink layer of printed food packaging into food (Henker *et al.*, 2013). The aim of this study was to answer two questions by means of typical examples: 1) Are nanoscale pigment particles present in the wet ink or in the dried ink film, as separate particles? 2) Is there any detectable migration of nanoscale particles into food? Offset printed cartons and gravure-printed polypropylene films were examined as model cases. The pigments present in the inks were copper phthalocyanine, titanium dioxide and aluminium. Measurements of the particle distribution on dispersed pigments by means of laser diffraction analysis showed that the printing ink with copper phthalocyanine contained about 50 vol% of the pigment particles of < 100 nm. In contrast, the respective laser diffraction analysis of the solvent-borne white printing ink TD White FD showed no evidence of TiO2 particles < 100 nm. These results were consistent with the pigment manufacturers' information that TiO2 pigments for printing inks are regulated to a range of about 200–400 nm in order to achieve optimal light scattering and, consequently, maximum opacity (note that the sized refers to the particles in the suspension and not necessarily the primary particles). By photon-correlation spectroscopic analysis, the measured average particle size was 80–90 nm for copper phthalocyanine and 200–300 nm for titanium dioxide. However, in the scanning electron microscopic cross-section, titanium oxide particles in the range of < 100 nm were provable. According to the authors, it can be assumed that TiO_2 pigments normally used in printing inks are not within the scope of the term "nanomaterial" in accordance with the Commission Recommendation, but still contain a percentage of nano-objects. The used platelet-shaped aluminium pigments had an average thickness of 30–40 nm and, therefore, must also be considered clearly as nanomaterial.

Detailed surface analysis of the printed matter e.g. by time-of-flight secondary ion mass spectroscopy (TOFSIMS) demonstrated that the nanoscale objects were completely embedded in the polymer matrix of the printed and dried ink films, i.e. they were completely covered with binder material. Following the wide range of analytical methods, no migration of nanoscale pigment particles could be detected from ink layers of printed food packaging into the food. Based on this, the authors concluded that exposure of the consumer to nanoparticles from the dried and cured ink layers may be excluded.

Industry representatives contacted as part of this study have made reference to this German study as the best available study on releases of pigments from printed matter.

A study of printed matter as part of the Danish EPA's surveys of consumer products quantified the potential releases of volatile organic compounds emitted from printed matter, but not the exposure to inks in the printed matter (Hansen and Eggert, 2003).

Much literature on the occupational exposure to carbon black by the printing process is available, but this literature generally does not deal with potential consumer exposure by the use of the printed matter. The OECD SIDS (2006) concluded, on the basis of the monograph from the International Agency for Research on Cancer (IARC, 1996), that exposure to carbon black, *per se*, does not occur when it remains bound within a product matrix, such as rubber, ink or paint.

Environmental releases

Possible releases of free pigments to the environment from the printed matter in use are considered unlikely. During recycling of paper, a de-inking process removes the inks from the printed matter. However, this process will not be addressed further in this project as notification with the Danish Nanoproduct Register is triggered by release during normal and foreseeable consumer use and not by possible release of free nanomaterials during the waste handling stages.

Exposure routes

The potential routes for exposure to nanosized pigments in inks of printed matter are listed in Table 23. Please note that the exposures concern the cured inks of printed matter and not exposures by handling inks or by the printing process.

TABLE 23
POTENTIAL EXPOSURE TO NANOSIZED PIGMENTS IN INKS OF PRINTED MATTER

Inks of printed matter	
Exposure routes for consumer exposure	
Dermal exposure	Handling of printed matter may result in contact between the inks and the hands. As the pigments are embedded in a polymer matrix, release of free nanosized pigments from the printed matter is, however, considered unlikely.
Oral exposure	Oral exposure to free nanosized pigments from inks on printed matter is considered unlikely.
Inhalation exposure	Inhalation exposure to free nanosized pigments from inks on printed matter is considered unlikely.

Exposure routes for environmental exposure	
Environmental exposure via wastewater	A large fraction of printed matter (>50%) is being recycled. De-inking is an important process during the recycling process. De-inking removes the ink, coatings, adhesives and other impurities from the printed matter. The de-inking process results in the creation of sludge, which may results in emission of pigments via wastewater. However, as noted in the main text, such release would not be considered a release under normal and foreseeable consumer use.
Environmental exposure via air	In the use-phase, environmental exposure via air to free nanosized pigments is considered unlikely. The fraction of printed matter which is not recycled (<50%) is incinerated in municipal solid waste incinerators. Emissions of nanoscale pigments to air are considered unlikely.
Environmental exposure by other routes	If printed matter is deposited in landfills, the contained pigments may be subject to leaching from the degrading paper. However, since a large volume of printed matter is recycled and the rest is used as biofuel in municipal solid waste incinerators, this exposure route is considered unlikely. See comment under waste water in relation to release during waste handling.

4.6 Textiles

Overall, knowledge about pigments in textile applications in Denmark appears rather limited. There is little textile production left in Denmark, and very few Danish companies operate with textile dyeing and printing.

4.6.1 Market for the products for consumer applications

Production, import and export statistics

Production, import and export volumes in tonnes per year have not been available from the PRODCOM (production statistics) database. Data on import/export were extracted by combined nomenclature (CN) codes from the database of Statistics Denmark using all codes for articles of apparel and clothing accessories (Chapters 61 and 62 of the Combined Nomenclature, comprising 460 commodity groups). The total import of textiles in 2013 in Denmark was 144,600 tonnes and the export was 85,838 tonnes (probably re-export). Assuming that textile production within Denmark is negligible, this results in a consumption of about 59,000 tonnes of textiles in 2013.

There are no statistical data on how many of the clothing articles are treated with dyes or prints, but pigments are used in both textile printing and for dyeing. The following estimates have been obtained by communication with the industry; at least 50% of printed textiles on the market in Denmark are printed with pigments, possibly even a higher fraction. With respect to dyed textiles, 40% can be expected to be dyed with pigments, while the remaining fractions are made up of other dyes.

4.6.2 Pigments in the products

Pigments are used in textile printing and dyeing. Both organic and inorganic pigments are used in textiles, either separately or in combination.

The data from the Productregister on pigments in inks described in section 4.5.2 would also cover inks for textile printing, but considering the comparatively minor manufacture of textiles in Denmark, inks for textile printing are considered a small fraction of the total. Pigments specifically indicated in the Productregister as used for manufacture of textiles are confidential, but the total is 0.02 t/y.

A survey of chemicals in textiles undertaken for the Danish EPA lists the pigments shown in Table 24 for use in textiles (Larsen *et al.*, 2000). These pigments are also currently the most used ones in textiles printing and dyeing, according to information from industry.

Organic pigments comprise azo-pigments, naphtols, perylentetracarboxyles, anthraquinones, dioxacines, and quinacridones, as well as halogenated copper-phtalocyanine compounds. The most common inorganic pigments in textiles are iron oxides, titanium oxides, aluminium powders, copper and zinc alloys, and carbon black (Larsen *et al.*, 2000).

TABLE 24
PIGMENTS COMMONLY USED IN TEXTILES (LARSEN *ET AL.* 2000).

Chemical group	C.I.-no.	CAS No [coming]
Organic pigments		
Azo-pigments (arylides, monoazo, di-azopyrazoloner)	Pigment Yellow 13 Pigment Yellow 14 Pigment Yellow 17 Pigment Yellow 74 Pigment Yellow 83 Pigment Yellow 155 Pigment Orange 34	5102-83-0 5468-75-7 4531-49-1 6358-31-2 5567-15-7 68516-73-4 15793-73-4
Naphtols	Pigment Orange 2	6410-09-9
Quinacridones	Pigment Red 122	980-26-7; 12225-00-2; 155328-35-1; 221658-08-8; 287098-90-2; 308795-57-5; 518035-23-9; 57917-17-6; 865272-16-8; 16043-40-6
Isoindolinones (azo methines, methines)	Pigment Yellow 110 Pigment Yellow 139	5590-18-1 36888-99-0
Copper-phtalocyanine compounds	Pigment Green 7 Pigment Black 15 Pigment Black 15:1 Pigment Black 15:3	1328-53-6 1317-38-0;1344-70-3 1317-33-5 1317-38-0;1344-70-3
Dioxaziner	Pigment Violet 23	215247-95-3
Inorganic pigments		
Carbon Black	Pigment Black 7	98615-67-9; 97793-37-8; 81180-26-9; 82600-58-6; 87934-03-0
Titanium oxide	Pigment White 6	13463-67-7; 1317-80-2; 1317-70-0

Pigment use for vat dyes

The differentiation of textile colorants into pigments and dyes is not always straightforward, since dyes can also be based on pigments. Pigments are, for example, the basis for vat dyes (in Danish: kypefarvestoffer, e.g. indigo). The final classification as dyes depends on the change in solubility due to a chemical modification which, in turn, influences the interaction with the fibre.
Vat dyes are preparations which consist of a vattable [4] colour pigment and a dispersing agent. Vat dyes are used in both textiles printing and dyeing, primarily in natural fibres such as cotton. They

[4] "Vattable" means that an insoluble pigment becomes a water-soluble dye by reduction in alkaline media, allowing for fixation on the fibre, whereafter they are converted back to the insoluble form by oxidation (Lacasse and Baumann,).

can be supplied in powder, granules, and paste form and provide a very high degree of colour fastness (Lacasse and Baumann, 2004). Because pigments used in vat dyes are made water-soluble by reduction in alkaline conditions during the dying process connecting them to the fibre, they are not present in the final products as particles, and not within the scope of the Nanoproduct Register and this report.

Disperse dyes
Disperse dyes are water-insoluble dyes mainly used in synthetic fibres such as polyester and polyamide. The name derives from the fact that the dyes are dispersed rather than fully dissolved in water (IARC, 2010). Even though they are insoluble in water, these substances are considered a particular type of dye as they are soluble in the hydrophebic polymer matrix. The dyes are "dissolved" in the polymer matrix at high temperatures, causing the pigments to subliminate and melt into the polymer. The dyes are not present in the matrix as particles and consequently cannot be released again as “free” particles.

Other use of pigments
Pigments are widely used in the textile printing and dyeing processes. The pigments are fixed to the fibre surface with the help of a binder. The binder is an aqueous dispersion of polymers, copolymers, or a polymer blend, e.g. polyacrylate, polystyrene, or polyurethane. Cross-linking occurs during heating. The type and amount of binder used depends on the amount of pigment required and has an impact on the feel, rubfastness and wetfastness of the dyeing (Lacasse and Baumann, 2004).

Pigment dyeing can be universally used for both synthetic and natural fibres; its application is found in heavy textiles (canvas), dress materials, shirting, bed linen and furnishing articles (Lacasse and Baumann, 2004).

Pigments in pigment printing are applied in dispersions containing 25 – 50% pigments and various additives (e.g. emulsifiers and dispersing agents) (Lacasse and Baumann, 2004). Pigment printing can likewise be applied to all kinds of fibres, and is often a cheaper way of colouring than dyeing. In contrast to dyed textiles, the handle of printed textiles becomes stiffer due to the polymer film on the fibre surface (Larsen *et al.*, 2000). Around 2000, about 50% of the printed textiles sold in Denmark were printed with inks containing pigments (Larsen *et al.*, 2000). It is not indicated how much of the textiles are currently printed.

Larsen *et al.* (2000) indicate that pigments account for 0,5-3% of the weight of printed textiles.

4.6.3 Potential for consumer and environmental exposure

Potential for releases of pigments from textiles
No literature on release of nanosized pigments from textiles has been identified.

Poulsen *et al.* (2011) evaluated the release of several metals, which may be contained in pigments, during washing. Since the origin of the metals (pigment/dye or other source) is not clearly identified, the evaluations cannot be used to conclude regarding release of pigments during washing.

According to communication with industry and research institutions, pigments are not released as “free” pigments from the textiles, since they are firmly fixed to/within the fibre. They will therefore only be released during washing and abrasion together with the matrix they are bound to, i.e. the binder system or the fibre. The resistance of the binder against washing, UV degradation, abrasion, etc. depends on the chemical type and quality of the binder. More expensive binders are commonly more resistant to crocking and washing, since they are softer and more flexible, thus also resulting in softer textile handling (Stenhaug, 2014).

This assessment is supported by a recent study on TiO_2-pigment release from functional, mainly synthetic textiles (Windler *et al.*, 2012). The pigments were found to be bound within the polymer fibre, resulting in low releases of 0.01 – 0.06% per wash cycle in 5 out of 6 tested textiles. One textile had a higher release fraction, which was explained by the presence of TiO_2 in a biocide and not as a pigment for colouring. Regardless of whether the TiO_2 had been added as a nanoparticle or not, the textiles did release some of the TiO2 in the nanoparticulate range, although most of it was in the form of agglomerates. The analyses showed that the TiO_2-fraction below 260 nm (containing the nanoparticulate fraction) was between 0.5 and 14% of the total released TiO_2.

As part of the Danish EPA's surveys of consumer products, Egmose and Pors (2005) analysed chemical substances in textile colorants for home use and Hansen (2005) studied the possible health effects from chemical substances in the colorants. The studies did not address the possible exposures of the consumers to pigments in the final textiles.

Exposure routes
The potential routes for exposure to pigments in particle form released from textiles are listed in Table 25. Please note that the table addresses exposures to pigments in the final textiles and not from the handling of the textile colorants or manufacture of textiles.

The conclusion, that the exposure to free nanosized pigments is unlikely, cannot be interpreted to mean that the use of hazardous pigment (e.g. based on heavy metals) could not result in any risk to consumers.

TABLE 25
POTENTIAL EXPOSURE TO NANOSIZED PIGMENTS IN TEXTILES

Textiles	
Exposure routes for consumer exposure	
Dermal exposure	Dermal exposure may occur during wearing of textile articles that are worn next to the skin. However, the release of free pigments during normal use is estimated to be negligible as the pigments are bound in a matrix or embedded in the fibres.
Oral exposure	Oral exposure to free pigments from textiles is considered unlikely. Children with mouthing behaviour may suck on a part of the clothes, but the released pigments (if any) are considered to be embedded in a matrix.
Inhalation exposure	Oral exposure to free pigments from textiles is considered unlikely.
Exposure routes for environmental exposure	
Environmental exposure via wastewater	The main route for environmental exposure to free pigments in textiles is considered to occur via wastewater from textile printing and dyeing processes. Pigments may be released from textiles during domestic washing, but sufficient data on whether the pigments are released as “free pigments” or bound within the binder or the fibre particles could not be identified. Some (organic) pigments may be degraded, but degradation is assumed to be substantially slower than for dyes (Larsen *et al.*, 2000).
Environmental exposure via air	Environmental exposure via air to free pigments from textiles is considered unlikely, since pigments are not volatile.
Environmental exposure by other routes	If used textiles are deposited in landfills, the contained pigments may be subject to leaching from the degrading textiles. However, this is not a relevant/likely exposure pathway in Denmark, where textiles are usually recycled or incinerated.

4.7 Rubber parts that contain carbon black

Carbon black in rubber is specifically exempt from notification with the Danish Nanoproduct Register via the following exemption:

- Articles of rubber, or rubber parts of articles, that contain the nanomaterials carbon black or silicon dioxide.

It can be discussed as to whether carbon black in rubber would have been out of scope of notification in any case, especially if the nanomaterial is not released as such (as a free nanomaterial), but released as a part of a rubber particle/matrix. Consequently, carbon black in rubber could also be argued to be out of scope of the current project, which mainly focuses on products which would have been registered if not specifically exempt. It was, however, decided that carbon black in rubber would be included in this project nonetheless.

Carbon black has other functions apart from acting as a pigment; the majority is used for reinforcement of rubber. This project generally focuses on pigments; however, as not only pigment use of carbon black in rubber is exempt, it was decided to focus not only on carbon black used as pigment, but also on general use of carbon black in rubber which might end up in consumer products.

A decision was made to focus on the main applications of carbon black based on surveys/assessments published by IARC, OECD, and Health and Environment Canada.

4.7.1 Market for the products for consumer applications

The global carbon black market capacity is eight to ten million tonnes (OECD, 2006; IARC, 2010); about 70% of this volume is used for reinforcement of tyres (cars, trucks, buses, agricultural vehicles and within in the aircraft sector) and about 20% is used in other rubber/elastomer products (OECD, 2006; IARC, 2010).

Of the remaining 10% carbon black amount, the largest use is in plastics, as colorants, UV-light stabilisers, strength-impairing fillers or electrical conductivity additives (Health and Environment Canada, 2013).

Further statistics on the split of carbon black uses share among "other rubber products" have not been identified, but cover a wide range of products including: Conveyer belts, hoses, tubes, rubber profiles, O-rings, roofing, covers for wire and cables, coated fabrics, gaskets, packaging, gloves, footwear, floor mats, tape, hard rubber products, pontoons and others (OECD, 2006; IARC, 2010; Health and Environment Canada, 2013). This list includes many consumer products; thus, carbon black is prevalent in a range of consumer products.

It can be noted that carbon black is on the EU positive list for use in plastic food packaging materials under certain restrictions as specified in Annex I of Commission Regulation 10/2011. Similarly, Health and Environment Canada (2013) notes that certain types of carbon black are allowed for use in food packaging in Canada.

4.7.2 Potential for consumer and environmental exposure

Except for tyres, the literature reviewed in this project generally does not address amounts in and release from rubber products.

Carbon black constitutes approx. 22% by weight of tyres (OECD, 2006; Health and Environment Canada, 2013). Carbon black is added to reinforce the tyres to reduce abrasion, tear, fatigue and flexing (IARC, 2010). Nevertheless, tyres typically lose 10% - 20% by weight during their life cycle and could thus present a potential source of exposure to carbon black (Health and Environment Canada, 2013).

Health and Environment Canada (2013), however, considers that release of unbound carbon black from tyres is unlikely as carbon black is released within elastomeric complexes, and migration of carbon black from this elastomer matrix is unlikely given its negligible solubility and volatility. The same is considered to apply to shredded tyres. It is further noted that tyre debris is typically >10 μm and thus not respirable.

Carbon black might be released during energy recovery from tyres/rubber or during accidental fires, which, however, are outside the scope of the Danish Nanoproduct Register focusing on releases from the consumer use phase.

5. Pigments in products not exempt from notification

Extracts for the pigments registered with the Danish Productregister also contained information on pigments used in products which would likely fall under the notification requirements of the Danish Nanoproduct Register. Furthermore, some of the projects undertaken as part of the Danish EPA's programme on chemical substances in consumer products include some information on pigments in the products.

This information should be seen as an aid to companies importing these types of products in relation to figuring out whether pigments are contained in their products, potentially leading to notification requirements. It should be stressed that these products might contain other pigments and/or other nanomaterials; thus, the lists presented in this report are not complete. Furthermore, pigments occurring in fewer than three products cannot be included for confidentiality reasons.

Data has been sought in the Productregister and the consumer product reports for the following products:

- Paints (should be notified if pigments are added with the intention to provide properties other than solely for colouring)
- Printing inks (e.g. cartridges for inkjet printers or laser printers used by consumers).
- Inks for fountain pens and various types of pens such as ballpoint pens, felt tips, marker-pens, etc.
- Cleaning agents (e.g. pigmented soft soap for pigmenting of floors).
- Printing inks for textile printing and textile colourants for home use.
- Modelling wax, "slimy" toys and similar products for children.
- Candles (if nanosized pigments are released as such during use).
- Shoe care products and other products for colouring leather.
- Pigments and pigment preparations for colouration of construction materials and coloured mortar.

The lists are included in Appendix 6.

6. Conclusion

Pigments *vis-à-vis* the EU nano definition
The main conclusions of the survey can be summarised as follows:

- Even now, no common ground has been established in relation to sampling and analytical methods to be used for determining the particle size distribution of pigments and, consequently, no final conclusions have been reached regarding determination of pigments as nanomaterials or not.

- Available information indicates that most pigments may likely be candidates for being considered nanomaterials on the basis of the size distribution of the constituent particles.

- Pigment preparations are manufactured in different grades from pigment powder with similar constituent particle size distribution, but the dispersed pigments in the preparations have different levels of aggregation and agglomeration.

- The data provided by technical data sheets and registrations on volumetric size distribution of pigments can generally not be used to determine whether the pigment should be considered a nanomaterial.

- For some applications, ultrafine pigments with particle size distributions in the commercial product in the nano-range are used. Examples of applications of ultrafine pigments are transparent coatings, some inks for digital printing and transparent plastic films.

- No pigments for particular applications have been identified which clearly fall outside the EU nano definition.

Pigments in exempt consumer products
The main conclusions of the survey as to exposure to free nanosized pigments released from the exempt products are summarised in the table below. Pigments released from painted products, printed matter and textiles are generally considered to be bound in a polymer matrix, and the pigments are therefore generally not released as free nanoparticles.

TABLE 26
SUMMARY OF POTENTIAL EXPOSURE TO FREE NANOSIZED PIGMENTS RELEASED FROM THE EXEMPT PRODUCTS

Products	Consumer exposure			Environmental exposure		
	Dermal	Oral	Inhalation	Waste water	Air	Other
Paint, lacquers and varnishes	X (application of mixtures)	-	X (application of mixtures)	X (cleaning of tools)	X (spraying outdoors)	X (soil, spill)
Adhesives, sealants, putty and filling materials	X (application of mixtures)	-	x (spaying of adhesives)	X (cleaning of tools)	-	X (soil, spill)
Inks on printed matter	-	-	-	?	-	-
Textiles	-	-	-	?	-	? (recycling)
Rubber products	-	-	-	-	-	-

Main data gaps
The main data gaps of importance for the conclusions drawn are:

- It remains that no common ground has been established in relation to sampling and analytical methods to be used for determining the particle size distribution of pigments.
- Number particle size distributions of constituent particles (as used in the EU nano definition) are not available for commercial products.
- The extent to which free pigments are released by washing of textiles and recycling of printed matter is unclear.
- The extent to which free pigments are actually released from paints, lacquers and varnishes and of adhesives, sealants, putty and filling materials during use; especially by inhalation but also by dermal contact, is unclear.

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Appendix 1: Abbreviation and acronyms

C.I.	Colour Index
CAS	Chemical Abstract Service
CEPE	European Council of the Paint, Printing Inks and Artists Colours Industry
CLP	Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures
CN	Combined nomenclature
CPMA	Color Pigments Manufacturers Association (U.S.A.)
DFL	The Danish Paint and Adhesives Industry
DLS	Dynamic Light Scattering
ECHA	European Chemicals Agency
EFCC	European Federation for Construction Chemicals
EM	Electron Microscopy
EPA	Environmental Protection Agency
ETAD	The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers
EU	European Union
FEICA	Association of the European Adhesive & Sealant Industry
FP7	Seventh Framework Programme
FSO	The Danish Sealants Association
IP	Inorganic Pigment
JRC	European Commission Joint Research Centre
LCD	Liquid Crystal Display
PRODCOM	Manufacturers sales by products statistics
REACH	Registration, Evaluation, Authorisation and restriction of Chemicals (Regulation (EC) No 1907/2006)
SEM	Scanning Electron Microscopy
SPERC	Specific Environmental Release Category
SPIN	Substances in Products in Nordic Countries (Database of the Nordic Product Registers)
TEM	Transmission electron microscopy
UC62	Use Categories (62 categories used in SPIN)
UCn	Use Categories National (Danish codes used in the Danish Productregister)
VdL	German Paint and Printing Ink Association

Appendix 2: Registered pigments

Data on registered pigments as indicated at the dissemination database at ECHA's website (ECHA, 2014). The information on colour index numbers is either based on the registrations, information from the consortia or various other sources.

For pigments registered by the Inorganic Pigments (IP) Consortium information on uses is provided by the Consortium (IP consortium, 2014). The table furthermore include pigments planned to be registered by 2018 by the IP Consortium (2014).

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
Substances registered by the Inorganic Pigment (IP) Consortium													
232-353-3	8007-18-9	Antimony nickel titanium oxide yellow	(Ni,Ti,Sb)O2	1,000 - 10,000	C.I. 77788	X		X			X	X	
232-382-1	8012-00-8	Pyrochlore, antimony lead yellow	Pb3(SbO4)3 á Pb(SbO3)2	10 - 100	C.I.77588			X			X		
235-790-8	12737-27-8	Chromium iron oxide	(Fe,Cr)2O3	10,000 - 100,000	C.I. 77500	X		X			X	X	
269-047-4	68186-85-6	Cobalt titanate green spinel	(Co)2TiO4	10 - 100	C.I. 77377	X		X			X	X	
269-049-5	68186-87-8	Cobalt zinc aluminate blue spinel	(Co,Zn)Al2O 4	100 - 1,000	C.I.77347	X		X			X	X	
269-050-0	68186-88-9	Zinc iron chromite brown spinel	(Zn,Fe)(Fe,C r)2O4	1,000 - 10,000	C.I.77503	X		X			X	X	X
269-052-1	68186-90-3	Chrome antimony titanium buff rutile.	(Ti,Cr,Sb)O2	10,000 - 100,000	C.I.77310	X		X			X	X	X
269-053-7	68186-91-4	Copper chromite black spinel	CuCr2O4	1,000+	C.I.77428	X		X			X	X	
269-054-2	68186-92-5	Chrome tungsten titanium buff rutile.	(Ti,Cr,W)O2	100 - 1,000	C.I. 77897	X		X			X		
269-056-3	68186-94-7	Manganese ferrite black spinel	(Fe,Mn)(Fe, Mn)2O4	1,000 - 10,000	C.I.77494	X		X			X	X	X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
269-057-9	68186-95-8	Zirconium vanadium blue zircon	(Zr,V)SiO4	100 - 1,000	-						X		
269-060-5	68186-97-0	Iron cobalt chromite black spinel	(Fe,Co)(Fe,Cr)2O4	1,000 - 10,000	C.I.77502			X			X	X	X
269-061-0	68186-99-2	Manganese alumina pink corundum	(Al,Mn)2O3	1,000 - 10,000	C.I.77005						X		
269-063-1	68187-01-9	Vanadium zirconium yellow baddeleyite	(Zr,V)O2	10 - 100	C.I.77991						X		
269-072-0	68187-11-1	Cobalt chromite blue green spinel	Co(Al,Cr)2O4	100 - 1,000	C.I.77343	X					X	X	
269-073-6	68187-12-2	Chrome tin pink sphene	CaO, SnO2, SiO2, Cr2O3	1,000 - 10,000	C.I.77301						X		
269-075-7	68187-15-5	Zirconium praseodymium yellow zircon	(Zr,Pr)SiO4	1,000 - 10,000				X			X		
269-093-5	68187-40-6	Olivine, cobalt silicate blue	Co2SiO4	1,000 - 10,000	C.I.77364						X		
269-103-8	68187-51-9	Zinc ferrite brown spinel	(Fe,Zn)Fe2O4	1,000 - 10,000	C.I.77496	X		X			X	X	X
270-185-2	68412-38-4	Manganese antimony titanium buff rutile	(Ti, Mn, Sb)O2	100 - 1,000	C.I.77899	X		X			X	X	
270-210-7	68412-79-3	Zirconium iron pink zircon	(Zr,Fe)SiO4	1,000 - 10,000	C.I.77996						X		
271-411-2	68555-06-6	Spinels, chromium iron manganese brown.	(Fe,Mn)(Fe, Cr,Mn)O4	100 - 1,000		X					X		
272-713-7	68909-79-5	Hematite, chromium green black	Cr2O3	1,000 - 10,000		X		X			X	X	
275-738-1	71631-15-7	Nickel iron chromite black spinel	(Ni,Fe)(Cr,Fe)2O4	1,000 - 10,000	C.I. 77504	X		X			X	X	
310-077-5	102184-95-2	Silicic acid, zirconium salt, cadmium pigment-encapsulated	Cd(S, Se) en ZrSiO4	100 - 1,000		X		X			X	X	

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
310-193-6	1345-16-0	Cobalt aluminate blue spinel	CoAl2O4	1,000 - 10,000	C.I.77346	X		X			X	X	
909-981-8 (List Number)		Reaction mass of fumes, silica and diiron trioxide	SiO2.Fe2O3	1,000 - 10,000							X	X	
936-897-9 (List Number)	1373399-58-6	Reaction mass of willemite, white and zinc iron chromite brown spinel	-	100 - 1,000		X		X			X	X	
Substances registered by the organic pigments (IP) consortia													
205-685-1	147-14-8	29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32 copper	C32H16CuN8	10,000 - 100,000	C.I. 74160 C.I. Pigment Blue 15:3	X	X		X				X
235-476-0	12239-87-1	copper chlorophthalocyanine	C32H15ClCuN8	1,000 - 10,000	C.I. 74250 Phthalocyanine Blue Bsx	X	X	X	X				X
248-573-8	27614-71-7	[tetrachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper	C32H12Cl4CuN8	100 - 1,000	C.I. 74250 Pigment Sky Blue								
215-524-7	1328-53-6	polychloro copper phthalocyanine	-	1,000 - 10,000	C.I. 74260. CI Pigment Blue 7	X	X	X	X				X
273-501-7	68987-63-3	Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, chlorinated	-	1,000 - 10,000	C.I.742520 C.I. Pigment Blue 76	X	X	X					X
238-238-4	14302-13-7	[1,3,8,16,18,24-hexabromo-2,4,9,10,11,15,17,22,23,25-decachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper	C32Br6Cl10CuN8	100 - 1,000	C.I. 74265; C.I. Pigment Green 36	X	X		X				X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
270-958-4	68512-13-0	Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, brominated chlorinated		100 - 1,000	C.I. 74265 C.I. Pigment Green 36		X	X					X
209-378-3	574-93-6	29H,31H-phthalocyanine	C32H18N8	100 - 1,000	C.I. 74100 C.I.Pigment Blue 16								
240-183-6	16040-69-0	[2,9,16,23-tetrachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper	C32H12Cl4CuN8	1 - 10	-	X	X						X
228-787-8	6358-85-6	2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[3-oxo-N-phenylbutyramide]	C32H26Cl2N6O4	10,000 - 100,000	C.I. 21090 C.I. Pigment Yellow 12	X	X		X				X
225-822-9	5102-83-0	2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(2,4-dimethylphenyl)-3-oxobutyramide]	C36H34Cl2N6O4	1,000 - 10,000	C.I. 21100 Pigment Yellow 13	X	X	X	X	X			X
226-789-3	5468-75-7	2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(2-methylphenyl)-3-oxobutyramide]	C34H30Cl2N6O4	1,000 - 10,000	C.I. 21095 C.I. Pigment Yellow 14	X	X	X					X
224-867-1	4531-49-1	2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(2-methoxyphenyl)-3-oxobutyramide]	C34H30Cl2N6O6	100 - 1,000	C.I. 21105 C.I. Pigment yellow 17	X	X	X	X				X
228-771-0	6358-37-8	2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(4-methylphenyl)-3-oxobutyramide]	C34H30Cl2N6O4	1 - 10	C.I. 21096 C.I. Pigment Yellow 55	X	X	X	X				X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
244-776-0	22094-93-5	2,2'-[(2,2',5,5'-tetrachloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(2,4-dimethylphenyl)-3-oxobutyramide]		10 - 100	C.I. 21127 Pigment Yellow 81	X							
226-939-8	5567-15-7	2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(4-chloro-2,5-dimethoxyphenyl)-3-oxobutyramide]	$C_{36}H_{32}Cl_4N_6O_8$	1,000 - 10,000	C.I. 21108; C.I. Pigment Yellow 83	X	X	X	X	X			X
290-823-3	90268-23-8	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[3-oxo-, N,N'-bis(p-anisyl and Ph) derivs.	-	10 - 100	C.I. 21101 PigmentYellow 126								
271-878-2	68610-86-6	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[3-oxo-, N,N'-bis(o-anisyl and 2,4-xylyl) derivs.		100 - 1,000	C.I. 21102 Pigment Yellow 127								
250-799-7	31775-20-9	2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(4-ethoxyphenyl)-3-oxobutyramide]	$C_{36}H_{34}Cl_2N_6O_6$	1 - 10	C.I. 21111 C.I.Pigment Yellow 74 C.I. Pigment Yellow 134 C.I. Pigment 152	X	X	X	X				X
279-017-2	78521-39-8	6-[[(4-methylphenyl)sulphonyl]amino]hexanoic acid	$C_{13}H_{19}NO_4S$	100 - 1,000	-								X
290-824-9	90268-24-9	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[3-oxo-, N,N'-bis(4-chloro-2,5-dimethoxyphenyl and 2,4-xylyl) derivs.	-	100 - 1,000	C.I. 21103 C.I. Pigment Yellow 176								

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
276-461-9	72207-62-6	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[3-oxo-, N,N'-bis(phenyl and 2,4-xylyl) derivs.		100 - 1,000	C.I. Pigment Yellow 188								
272-732-0	68910-13-4	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[3-oxo-, N,N'-bis(phenyl and o-tolyl) derivs.	-	10 - 100	-								
231-494-8	7585-41-3	barium 4-[(5-chloro-4-methyl-2-sulphonatophenyl)azo]-3-hydroxy-2-naphthoate	C18H13ClN2 O6S.Ba	100 - 1,000	C.I. 15865:1 C.I.Pigment Red 48:1	X	X	X	X				X
230-303-5	7023-61-2	calcium 4-[(5-chloro-4-methyl-2-sulphonatophenyl)azo]-3-hydroxy-2-naphthoate	C18H13ClN2 O6S.Ca	1,000 - 10,000	C.I. 15865:2 C.I. Pigment Red 48:2	X	X	X	X				X
239-879-2	15782-05-5	strontium 4-[(5-chloro-4-methyl-2-sulphonatophenyl)azo]-3-hydroxy-2-naphthoate (1:1)	C18H13ClN2 O6S.Sr	100 - 1,000	C.I. 15865:3 C.I. Pigment Red 48:3	X	X	X	X				X
226-102-7	5280-66-0	manganese, 4-[(5-chloro-4-methyl-2-sulfophenyl)azo]-3-hydroxy-2-naphthalenecarboxylic acid complex		10 - 100	C.I. 15865:4 Pigment Red 48:4	X	X	X					X
267-291-6	67828-72-2	strontium 4-[(4-chloro-5-methyl-2-sulphonatophenyl)azo]-3-hydroxy-2-naphthoate (1:1)	C18H13ClN2 O6S.Sr	1 - 10	C.I. 15860 C.I. Pigment Red 52								
241-793-5	17832-28-9	4-(vinyloxy)butan-1-ol	C6H12O2	Confidential	-								
235-471-3	12238-31-2	manganese, 4-[(4-chloro-5-methyl-2-sulfophenyl)azo]-3-hydroxy-2-naphthalenecarboxylic acid complex		1 - 10	C.I. 15860:2 Pigment Red 52:2	X	X	X					X
226-109-5	5281-04-9	calcium 3-hydroxy-4-[(4-methyl-2-sulphonatophenyl)azo]-2-naphthoate	C18H14N2O 6S.Ca	10,000 - 100,000	C.I. 15850:1 C.I. Pigment Red 57:1	X	X	X	X				X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
259-587-9	55310-46-8	sodium dibenzyldithiocarbamate	C15H15NS2.Na	1,000 - 10,000	-								X
277-552-6	73612-29-0	strontium 3-hydroxy-4-[(4-methyl-2-sulphonatophenyl)azo]-2-naphthoate	C18H14N2O6S.Sr	100 - 1,000	-	X	X	X	X				
213-879-2	1047-16-1	5,12-dihydroquino[2,3-b]acridine-7,14-dione	C20H12N2O2	1,000 - 10,000	C.I. 46500 C.I. Pigment Violet 19	X	X	X	X				X
213-561-3	980-26-7	5,12-dihydro-2,9-dimethylquino[2,3-b]acridine-7,14-dione	C22H16N2O2	1,000 - 10,000	C.I. 73915 C.I. Pigment Red 122	X	X	X	X				X
221-424-4	3089-17-6	2,9-dichloro-5,12-dihydroquino[2,3-b]acridine-7,14-dione	C20H10Cl2N2O2	100 - 1,000	C.I. 73907 C.I. Pigment Red 202	X	X	X					
254-100-6	38720-66-0	dichloro-5,12-dihydroquino[2,3-b]acridine-7,14-dione	C20H10Cl2N2O2	10 - 100	-								
221-423-9	3089-16-5	4,11-dichloro-5,12-dihydroquino[2,3-b]acridine-7,14-dione	C20H10Cl2N2O2	10 - 100	-								
228-768-4	6358-31-2	2-[(2-methoxy-4-nitrophenyl)azo]-N-(2-methoxyphenyl)-3-oxobutyramide	C18H18N4O6	1,000 - 10,000	C.I. 11741 C.I. Pigment Yellow 74	X	X	X	X				X
228-767-9	6358-30-1	8,18-dichloro-5,15-diethyl-5,15-dihydrodiindolo[3,2-b:3',2'-m]triphenodioxazine	C34H22Cl2N4O2	1,000 - 10,000	C.I. 51319 C.I. Pigment Violet 23	X	X						
229-440-3	6535-46-2	3-hydroxy-N-(o-tolyl)-4-[(2,4,5-trichlorophenyl)azo]naphthalene-2-carboxamide	C24H16Cl3N3O2	1,000 - 10,000	C.I. 12370 C.I. Pigment Red 112								

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
266-564-7	67075-37-0	2,9-bis(2-phenylethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone	C40H26N2O4	10 - 100	C.I. 71132 C.I Pigment Black 31	X	X	X					X
280-472-4	83524-75-8	2,9-bis(p-methoxybenzyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone	C40H26N2O6	10 - 100	C.I. 71133 C.I Pigment Black 32	X	X	X					X
201-375-5	81-77-6	6,15-dihydroanthrazine-5,9,14,18-tetrone	C28H14N2O4	100 - 1,000	C.I. 69800 C.I Pigment Blue 60	X	X	X					X
252-772-5	35869-64-8	N,N'-(2-chloro-1,4-phenylene)bis[4-[(4-chloro-2-nitrophenyl)azo]-3-hydroxynaphthalene-2-carboxamide]	C40H23Cl3N8O8	100 - 1,000	C.I. 20060 C.I Pigment Brown 23	X	X	X					X
230-258-1	6992-11-6	4-[(2,5-dichlorophenyl)azo]-N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-hydroxynaphthalene-2-carboxamide	C24H15Cl2N5O3	10 - 100	C.I. 12510 C.I Pigment Brown 25								
201-344-6	81-33-4	perylene-3,4:9,10-tetracarboxydiimide	C24H10N2O4	100 - 1,000	C.I. 71129 C.I.Pigment Violet 29	X	X	X					X
271-178-7	68516-75-6	N,N'-naphthalene-1,5-diylbis[4-[(2,3-dichlorophenyl)azo]-3-hydroxynaphthalene-2-carboxamide]	C44H26Cl4N6O4	10 - 100	C.I. Pigment Brown 41								
222-429-4	3468-63-1	1-[(2,4-dinitrophenyl)azo]-2-naphthol	C16H10N4O5	100 - 1,000	C.I. 12075 C.I Pigment Orange 5	X	X	X					
222-530-3	3520-72-7	4,4'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one]	C32H24Cl2N8O2	100 - 1,000	C.I. 21110 C.I Pigment Orange 13	X	X	X					

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
239-898-6	15793-73-4	4,4'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[2,4-dihydro-5-methyl-2-(p-tolyl)-3H-pyrazol-3-one]	C34H28Cl2 N8O2	100 - 1,000	C.I. 21115 C.I Pigment Orange 34	X	X	X					X
235-462-4	12236-62-3	2-[(4-chloro-2-nitrophenyl)azo]-N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxobutyramide	C17H13ClN6 O5	100 - 1,000	C.I. 11780 C.I Pigment Orange 36	X	X	X					X
235-464-5	12236-64-5	N-[4-(acetylamino)phenyl]-4-[[5-(aminocarbonyl)-2-chlorophenyl]azo]-3-hydroxynaphthalene-2-carboxamide	C26H20ClN 5O4	10 - 100	C.I. 12367 C.I Pigment Orange 38								
267-122-6	67801-01-8	barium bis[5-chloro-4-ethyl-2-[(2-hydroxy-1-naphthyl)azo]benzenesulphonate]	C18H15ClN2 O4S.1/2Ba	1 - 10	C.I. 15602 C.I Pigment Orange 46	X	X	X					X
277-823-9	74336-59-7	3-[(4-chloro-2-nitrophenyl)azo]-2-methylpyrazolo[5,1-b]quinazolin-9(1H)-one	C17H11ClN6 O3	100 - 1,000	C.I. 12915 C.I Pigment Orange 67	X	X	X					X
227-930-1	6041-94-7	4-[(2,5-dichlorophenyl)azo]-3-hydroxy-N-phenylnaphthalene-2-carboxamide	C23H15Cl2 N3O2	1,000 - 10,000	C.I. 12310 C.I Pigment Red 2	X	X	X					X
219-372-2	2425-85-6	1-(4-methyl-2-nitrophenylazo)-2-naphthol	C17H13N3O 3	10 - 100	C.I. 12120 C.I Pigment Red 3	X	X	X					
220-562-2	2814-77-9	1-[(2-chloro-4-nitrophenyl)azo]-2-naphthol	C16H10ClN 3O3	100 - 1,000	C.I. 12085 C.I Pigment Red 4	X	X	X					X
229-107-2	6410-41-9	N-(5-chloro-2,4-dimethoxyphenyl)-4-[[5-[(diethylamino)sulphonyl]-2-methoxyphenyl]azo]-3-hydroxynaphthalene-2-carboxamide	C30H31ClN 4O7S	10 - 100	C.I. 12490 C.I Pigment Red 5								

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
229-102-5	6410-32-8	3-hydroxy-4-[(2-methyl-4-nitrophenyl)azo]-N-(o-tolyl)naphthalene-2-carboxamide	C25H20N4 O4	10 - 100	C.I. 12385 C.I Pigment Red 12								
229-314-8	6471-50-7	4-[(4-chloro-2-nitrophenyl)azo]-3-hydroxy-N-(2-methylphenyl)naphthalene-2-carboxamide	C24H17ClN 4O4	1 - 10	C.I Pigment Red 14								
229-245-3	6448-95-9	3-hydroxy-4-[(2-methyl-5-nitrophenyl)azo]-N-phenylnaphthalene-2-carboxamide	C24H18N4O 4	1 - 10	C.I. 12315 C.I Pigment Red 22	X	X	X					
228-788-3	6358-87-8	diethyl 4,4'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[4,5-dihydro-5-oxo-1-phenyl-1H-pyrazole-3-carboxylate]	C36H28Cl2 N8O6	10 - 100	C.I. 21120 C.I Pigment Red 38			X					
214-160-6	1103-38-4	barium bis[2-[(2-hydroxynaphthyl)azo]naphthalenesulphonate]	C20H14N2O 4S.1/2Ba	1 - 10	C.I. 15630:1 C.I Pigment Red 49:1	X	X	X					X
277-335-6	73263-40-8	strontium bis[2-chloro-5-[(2-hydroxy-1-naphthyl)azo]toluene-4-sulphonate]	C17H13ClN2 O4S.1/2Sr	1 - 10	C.I. 15585:3 C.I Pigment Red 53:3	X	X	X					X
277-553-1	73612-34-7	barium bis[6-chloro-4-[(2-hydroxy-1-naphthyl)azo]toluene-3-sulphonate]	C17H13ClN2 O4S.1/2Ba	1 - 10	C.I Pigment Red 69	X	X	X					X
226-106-9	5280-78-4	N,N'-(2-chloro-1,4-phenylene)bis[4-[(2,5-dichlorophenyl)azo]-3-hydroxynaphthalene-2-carboxamide]	C40H23Cl5 N6O4	100 - 1,000	C.I. 20735 C.I Pigment Red 144	X	X	X					X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
226-103-2	5280-68-2	N-(4-chloro-2,5-dimethoxyphenyl)-3-hydroxy-4-[[2-methoxy-5-[(phenylamino)carbonyl]phenyl]azo]naphthalene-2-carboxamide	C33H27ClN4O6	100 - 1,000	C.I. 12485 C.I Pigment Red 146	X	X	X					
269-389-4	68227-78-1	N-(5-chloro-2-methylphenyl)-3-hydroxy-4-[[2-methoxy-5-[(phenylamino)carbonyl]phenyl]azo]naphthalene-2-carboxamide	C32H25ClN4O4	1 - 10	C.I. 12433 C.I Pigment Red 147								
225-590-9	4948-15-6	2,9-bis(3,5-dimethylphenyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone	C40H26N2O4	100 - 1,000	C.I. 71137 C.I Pigment Red 149	X	X	X					X
223-460-6	3905-19-9	N,N'-phenylene-1,4-bis[4-[(2,5-dichlorophenyl)azo]-3-hydroxynaphthalene-2-carboxamide]	C40H24Cl4N6O4	100 - 1,000	C.I. 20730 C.I Pigment Red 166								X
220-509-3	2786-76-7	4-[[4-(aminocarbonyl)phenyl]azo]-N-(2-ethoxyphenyl)-3-hydroxynaphthalene-2-carboxamide	C26H22N4O4	100 - 1,000	C.I. 12474 C.I Pigment Red 170	X	X	X					X
235-425-2	12225-06-8	N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-hydroxy-4-[[2-methoxy-5-[(phenylamino)carbonyl]phenyl]azo]naphthalene-2-carboxamide	C32H24N6O5	100 - 1,000	C.I. 12515 C.I Pigment Red 176								
223-754-4	4051-63-2	4,4'-diamino[1,1'-bianthracene]-9,9',10,10'-tetraone	C28H16N2O4	100 - 1,000	C.I. 65300 C.I Pigment Red 177	X	X	X	X	X			X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
221-264-5	3049-71-6	2,9-bis[4-(phenylazo)phenyl]anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone	C48H26N6 O4	100 - 1,000	C.I. 71155 C.I Pigment Red 178	X	X	X					X
226-866-1	5521-31-3	2,9-dimethylanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone	C26H14N2O 4	100 - 1,000	C.I. 71130 C.I Pigment Red 179	X	X	X					X
261-785-5	59487-23-9	4-[[5-[[[4-(aminocarbonyl)phenyl]amino]carbonyl]-2-methoxyphenyl]azo]-N-(5-chloro-2,4-dimethoxyphenyl)-3-hydroxynaphthalene-2-carboxamide	C34H28ClN 5O7	10 - 100	C.I. 12486 C.I Pigment Red 187								
263-272-1	61847-48-1	methyl 4-[[(2,5-dichlorophenyl)amino]carbonyl]-2-[[2-hydroxy-3-[[(2-methoxyphenyl)amino]carbonyl]-1-naphthyl]azo]benzoate	C33H24Cl2 N4O6	100 - 1,000	C.I. 12467 C.I Pigment Red 188								
250-800-0	31778-10-6	butyl 2-[[3-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-hydroxy-1-naphthyl]azo]benzoate	C29H25N5O 5	10 - 100	C.I. 12514 C.I Pigment Red 208								
255-005-2	40618-31-3	N,N'-(2,5-dichloro-1,4-phenylene)bis[4-[(2,5-dichlorophenyl)azo]-3-hydroxynaphthalene-2-carboxamide]	C40H22Cl6 N6O4	100 - 1,000	C.I. 200660 C.I Pigment Red 214	X	X	X					X
269-507-4	68259-05-2	bis(2-chloroethyl) 3,3'-[(2,5-dimethyl-p-phenylene)bis[iminocarbonyl(2-hydroxy-1,3-naphthylene)azo]]di-p-toluate	C50H42Cl2 N6O8	10 - 100	C.I. 20055 C.I Pigment Red 220	X	X	X					X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
204-905-3	128-69-8	perylene-3,4:9,10-tetracarboxylic dianhydride	C24H8O6	100 - 1,000	C.I. 71127 C.I Pigment Red 224								
257-776-0	52238-92-3	N,N'-(2,5-dichloro-1,4-phenylene)bis[4-[[2-chloro-5-(trifluoromethyl)phenyl]azo]-3-hydroxynaphthalene-2-carboxamide]	C42H22Cl4 F6N6O4	10 - 100	C.I Pigment Red 242								
401-540-3	84632-65-5	3,6-bis(4-chlorophenyl)-1H,2H,4H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione	-	1-10, 10-100	C.I. 56110 C.I Pigment Red 254								
253-292-9	36968-27-1	4-[[4-(aminocarbonyl)phenyl]azo]-3-hydroxy-N-(2-methoxyphenyl)naphthalene-2-carboxamide	C25H20N4 O4	1-10	C.I.12474 C.I Pigment Red 266								
268-028-8	67990-05-0	N-(5-chloro-2-methoxyphenyl)-3-hydroxy-4-[[2-methoxy-5-[(phenylamino)carbonyl]phenyl]azo]naphthalene-2-carboxamide	C32H25ClN 4O5	10 - 100	C.I 12466 C.I Pigment Red 269	X	X	X					
235-426-8	12225-08-0	N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-hydroxy-4-[[2,5-dimethoxy-4-[(methylamino)sulphonyl]phenyl]azo]naphthalene-2-carboxamide	C27H24N6O 7S	10 - 100	C.I. 12517 C.I Pigment Violet 32								
219-730-8	2512-29-0	2-[(4-methyl-2-nitrophenyl)azo]-3-oxo-N-phenylbutyramide	C17H16N4O 4	100 - 1,000	C.I 11680 C.I. Pigment Yellow 1	X	X	X					

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
229-355-1	6486-23-3	2-[(4-chloro-2-nitrophenyl)azo]-N-(2-chlorophenyl)-3-oxobutyramide	C16H12Cl2N4O4	100 - 1,000	C.I. 11710 C.I. Pigment Yellow 3	X	X	X					
235-557-0	12286-65-6	calcium bis[3-nitro-4-[[2-oxo-1-[(phenylamino)carbonyl]propyl]azo]benzenesulphonate]	C16H14N4O7S.1/2Ca	10 - 100	C.I. 13880 C.I. Pigment Yellow 61	X	X	X					
229-419-9	6528-34-3	2-[(4-methoxy-2-nitrophenyl)azo]-N-(2-methoxyphenyl)-3-oxobutyramide	C18H18N4O6	100 - 1,000	C.I. 11740 C.I. Pigment Yellow 65								
236-852-7	13515-40-7	2-[(4-chloro-2-nitrophenyl)azo]-N-(2-methoxyphenyl)-3-oxobutyramide	C17H15ClN4O5	100 - 1,000	C.I. 11738 C.I. Pigment Yellow 73								
226-970-7	5580-57-4	3,3'-[(2-chloro-5-methyl-p-phenylene)bis[imino(1-acetyl-2-oxoethylene)azo]]bis[4-chloro-N-(3-chloro-o-tolyl)benzamide]	C43H35Cl5N8O6	100 - 1,000	C.I. 20710 C.I Pigment Yellow 93	X	X	X					X
226-107-4	5580-58-5	3,3'-[(2,5-dimethyl-p-phenylene)bis[imino(1-acetyl-2-oxoethylene)azo]]bis[4-chloro-N-(5-chloro-o-tolyl)benzamide]	C44H38Cl4N8O6	100 - 1,000	C.I Pigment Yellow 94	X	X	X					X
249-955-7	29920-31-8	dimethyl 5-[[1-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-oxopropyl]azoterephthalate	C21H19N5O7	10 - 100	C.I. 11783 C.I Pigment Yellow 120								
253-256-2	36888-99-0	5,5'-(1H-isoindole-1,3(2H)-diylidene)dibarbituric acid	C16H9N5O6	1,000-10,000	C.I. 56298 C.I Pigment Yellow 139	X	X	X					X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
607-578-9	25157-64-6	2,4,6(1H,3H,5H)-Pyrimidinetrione, 5,5'-(1,2-diazenediyl)bis-	-	Intermediate Use Only	C.I Pigment Yellow 150								X
250-830-4	31837-42-0	2-[[1-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-oxopropyl]azo]benzoic acid	C18H15N5O5	100 - 1,000	C.I. 13980 C.I Pigment Yellow 151	X	X	X					
268-734-6	68134-22-5	N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxo-2-[[2-(trifluoromethyl)phenyl]azo]butyramide	C18H14F3N5O3	100 - 1,000	C.I. 13980 C.I Pigment Yellow 154	X	X	X					
271-176-6	68516-73-4	tetramethyl 2,2'-[1,4-phenylenebis[imino(1-acetyl-2-oxoethane-1,2-diyl)azo]]bisterephthalate	C34H32N6O12	100 - 1,000	C.I. 200310 C.I Pigment Yellow 155	X	X	X					X
276-057-2	71832-85-4	calcium bis[4-[[1-[[(2-chlorophenyl)amino]carbonyl]-2-oxopropyl]azo]-3-nitrobenzenesulphonate]	C16H13ClN4O7S.1/2Ca	10 - 100	C.I. 13960 C.I Pigment Yellow 168	X	X	X					X
252-650-1	35636-63-6	dimethyl 2-[[1-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-oxopropyl]azo]terephthalate	C21H19N5O7	10 - 100	C.I. 11784 C.I Pigment Yellow 175								
278-770-4	77804-81-0	2,2'-[ethylenebis(oxyphenyl-2,1-eneazo)]bis[N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxobutyramide	C36H32N10O8	100 - 1,000	C.I. 21290 C.I Pigment Yellow 180	X	X	X					
277-873-1	74441-05-7	N-[4-(aminocarbonyl)phenyl]-4-[[1-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-oxopropyl]azo]benzamide	C25H21N7O5	100 - 1,000	C.I. 11777 C.I Pigment Yellow 181								

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
265-634-4	65212-77-3	calcium 4,5-dichloro-2-[[4,5-dihydro-3-methyl-5-oxo-1-(3-sulphonatophenyl)-1H-pyrazol-4-yl]azo]benzenesulphonate	C16H12Cl2N4O7S2.Ca	100 - 1,000	C.I. 18792 C.I Pigment Yellow 183	X	X	X					X
278-388-8	76199-85-4	2-cyano-2-[2,3-dihydro-3-(tetrahydro-2,4,6-trioxo-5(2H)-pyrimidinylidene)-1H-isoindol-1-ylidene]-N-methylacetamide	C16H11N5O4	100 - 1,000	C.I. 56290 C.I Pigment Yellow 185	X	X	X					X
911-739-1	99402-80-9	Reaction mass of N-(4-chloro-2,5-dimethoxyphenyl)- 3-hydroxy-4-[[2-methoxy-5- [(phenylamino)carbonyl]phenyl]azo]naphthalene-2-carboxamide and N-(5-chloro-2-methylphenyl)-3-hydroxy-4-[[2-methoxy-5- [(phenylamino)carbonyl]phenyl]azo]naphthalene-2-carboxamide '	multi constituent substance	10 - 100	C.I. 12487 C.I Pigment Red 184								
911-436-4	61932-63-6	Reaction mass of 4-[[4-(aminocarbonyl)phenyl]azo]-N-(2-ethoxyphenyl)-3-hydroxynaphthalene-2-carboxamide and 4-[[4-(aminocarbonyl)phenyl]azo]-3-hydroxy-N-(2-methoxyphenyl)naphthalene-2-carboxamide	multi constituent substance	10 - 100	C.I. C.I. 12477 C.I Pigment Red 210								
258-221-5	52846-56-7	N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-2-[(4-nitrophenyl)azo]-3-oxobutyramide	C17H14N6O5	10 - 100	C.I. 11775 C.I Pigment Orange 62								

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
257-515-0	51920-12-8	N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-hydroxy-4-[[2-methoxy-5-methyl-4-[(methylamino)sulphonyl]phenyl]azo]naphthalene-2-carboxamide	$C_{27}H_{24}N_6O_6S$	10 - 100	C.I. 12516 C.I Pigment Red 185	X	X	X					
275-639-3	71566-54-6	diisopropyl 3,3'-[(2,5-dichloro-1,4-phenylene)bis[iminocarbonyl(2-hydroxy-3,1-naphthylene)azo]]bis[4-methylbenzoate]	$C_{50}H_{42}Cl_2N_6O_8$	10 - 100	C.I. 20065 C.I Pigment Red 221	X	X						X
279-211-7	79665-24-0	N,N'-(2,5-dimethyl-1,4-phenylene)bis[4-[(5-chloro-2-methylphenyl)azo]-3-hydroxynaphthalene-2-carboxamide	$C_{44}H_{34}Cl_2N_6O_4$	1-10	C.I Pigment Red 262								
600-736-8	106276-80-6	Benzoic acid, 2,3,4,5-tetrachloro-6-cyano-, methyl ester, reaction products with p-phenylenediamine and sodium methoxide	-	100 - 1,000	C.I Pigment Yellow 110	X	X	X					X
240-131-2	15993-42-7	N-(5-chloro-2-methoxyphenyl)-2-[(2-methoxy-4-nitrophenyl)azo]-3-oxobutyramide	$C_{18}H_{17}ClN_4O_6$	10 - 100	C.I.11745 C.I Pigment Yellow 111								
279-356-6	79953-85-8	3,3'-[(2-chloro-5-methyl-p-phenylene)bis[imino(1-acetyl-2-oxoethylene)azo]]bis[4-chloro-N-[2-(4-chlorophenoxy)-5-(trifluoromethyl)phenyl]benzamide]	$C_{55}H_{37}Cl_5F_6N_8O_8$	100 - 1,000	C.I. 20037 C.I Pigment Yellow 128	X	X	X					X
30125-47-4	30125-47-4	3,4,5,6-tetrachloro-N-[2-(4,5,6,7-tetrachloro-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-8-quinolyl]phthalimide	30125-47-4	100 - 1,000	C.I Pigment Yellow 138	X	X	X					X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
226-107-4	5280-80-8	3,3'-[(2,5-dimethyl-p-phenylene)bis[imino(1-acetyl-2-oxoethylene)azo]]bis[4-chloro-N-(5-chloro-o-tolyl)benzamide]	$C_{44}H_{38}Cl_4N_8O_6$	100 - 1,000	C.I. 20034 C.I Pigment Yellow 95	X	X	X					X
279-914-9	82199-12-0	N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-2-[(2-methoxyphenyl)azo]-3-oxobutyramide	$C_{18}H_{17}N_5O_4$	100 - 1,000	C.I. 11745 C.I Pigment Yellow 194								
Other inorganic pigments													
236-675-5	13463-67-7	titanium dioxide	TiO_2	1,000,000-10,000,000	C.I. 77891 C.I. Pigment White 6	X	X	X	X	X		X	X
215-282-2	1317-80-2	rutile (TiO_2)	Rutile (TiO_2)	10,000 - 100,000	C.I. 77891; C.I. Pigment White 6	X	X	X	X	X		X	X
215-222-5	1314-13-2	zinc oxide		100,000 - 1,000,000	C.I. 77947; C.I. Pigment White 4	X	X	X	X	X	X	X	X
215-251-3	1314-98-3	zinc sulphide	SZn	100,000 - 1,000,000	C.I. 77975 C.I. 77995 C.I. Pigment White 7	X	X	X	X	X			X
215-168-2	1309-37-1	diiron trioxide	Fe_2O_3	100,000 - 1,000,000	C.I. 77491 C.I. Pigment Red 101	X		X	X	X	X	X	X
257-098-5	51274-00-1	iron hydroxide oxide yellow	FeO_2H	100,000 - 1,000,000	C.I. 77492 C.I. Pigment Yellow 42	X	X	X	X	X		X	X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
215-277-5	1317-61-9	triiron tetraoxide	Fe3O4	100,000 - 1,000,000	C.I. Pigment Black 11	X	X	X	X	X		X	X
235-049-9	12062-81-6	iron manganese trioxide	FeMnO3	1,000 - 10,000	C.I. 77536 C.I. Pigment black 33	X	X	X	X	X		X	X
215-275-4	1317-60-8	hematite (Fe2O3)	Fe2O3	10,000 - 100,000	C.I. 77491 C.I. Pigment Red 101						X	X	X
215-609-9	1333-86-4	carbon black	-	1,100,000 - 11,000,000	C.I. 77266 C.I. Pigment Black 6 C.I. Pigment Black 7	X	X	X	X	X		X	X
235-759-9	12656-85-8	lead chromate molybdate sulfate red	-	1,000 - 10,000	C.I. 77605 C.I. Pigment Red 104	X		X	X				X
215-693-7	1344-37-2	lead sulfochromate yellow	PbCrO4+PbSO4	1,000 - 10,000	C.I. 77603 C.I. Pigment Yellow 34	X		X	X				X
215-267-0	1317-36-8	Lead monoxide	PbO	100,000 - 1,000,000	C.I. 77577 C.I. Pigment Red 105	X		X			X		X
232-382-1	8012-00-8	pyrochlore, antimony lead yellow	-	10 - 100	C.I. 77588 C.I. Pigment yellow 41	X	X				X		X
233-245-9	10099-74-8	lead dinitrate	Pb(NO3)2	10 - 100	-	X			X				X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
215-235-6	1314-41-6	orange lead	Pb3O4	10,000 - 100,000	C.I. 77578 C.I. Pigment Red 105	X		X			X		X
209-943-4	598-63-0	lead carbonate	CH2O3.Pb	Intermediate Use Only	-								
261-218-1	58339-34-7	cadmium sulfoselenide red	-	100 - 1,000	C.I. 77202 C.I.Pigment Red 108	X					X		X
215-160-9	1308-38-9	chromium (III) oxide	Cr2O3	10,000 - 100,000	C.I. 77288 C.I. Pigment Green 17	X	X	X			X	X	X
232-466-8	8048-07-5	cadmium zinc sulfide yellow	-	100 - 1,000	C.I. 77205 C.I. Pigment Yellow 35	X					X		X
233-257-4	10101-66-3	ammonium manganese(3+) diphosphate	H4O7P2.H3 N.Mn	10 - 100	C.I. 77742 C.I. Pigment Violet 16	X	X	X		X			X
237-898-0	14059-33-7	bismuth vanadium tetraoxide	BiO4V	1,000 - 10,000	C.I. 771740 C.I. Pigment Yellow 184	X	X	X					X
225-935-3	5160-02-1	barium bis[2-chloro-5-[(2-hydroxy-1-naphthyl)azo]toluene-4-sulphonate]	C17H13ClN2 O4S.1/2Ba	1,000 - 10,000	C.I. 15585:1 C.I. Pigment Red 53:1	X	X	X					X
264-885-7	64417-98-7	Yttrium zirconium oxide	-	100 - 1,000	-	X			X				X
309-928-3	57455-37-5	Silicic acid, aluminum sodium salt, sulfurized	-	10,000 - 100,000	C.I. 77007 C.I. Pigment Blue 29	X	X		X	X			X

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						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
Other organic pigments and multiconstitent substances													
235-427-3	12225-18-2	N-(4-chloro-2,5-dimethoxyphenyl)-2-[[2,5-dimethoxy-4-[(phenylamino)sulphonyl]phenyl]azo]-3-oxobutyramide	C26H27ClN4O8S	100 - 1,000	C.I. 11767 C.I. Pigment Yellow 97								
235-428-9	12225-21-7	aluminium, 4,5-dihydro-5-oxo-1-(4-sulfophenyl)-4-[(4-sulfophenyl)azo]-1H-pyrazole-3-carboxylic acid complex		1-10	C.I. 19140:1 C.I. Pigment Yellow 100								
235-468-7	12237-62-6	ferrate(4-), hexakis(cyano-C)-, methylated 4-[(4-aminophenyl)(4-imino-2,5-cyclohexadien-1-ylidene)methyl]benzenamine copper(2+) salts	-	100 - 1,000	C.I. 42535:3 C.I. Pigment Violet 27	X	X		X				X
235-558-6	12286-66-7	calcium bis[4-[[1-[[(2-methylphenyl)amino]carbonyl]-2-oxopropyl]azo]-3-nitrobenzenesulphonate]	C17H16N4O7S.1/2Ca	100 - 1,000	C.I. 13940 C.I.Pigment Yellow 62	X	X		X				X
239-888-1	15790-07-5	aluminium, 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid complex	-	1-10	C.I. 15985:1 C.I. Pigment Yellow 104								X
254-879-2	40306-75-0	3-acetamido-5-amino-4-hydroxybenzenesulphonic acid	C8H10N2O5S	10-100	-								
224-481-3	4378-61-4	4,10-dibromodibenzo[def,mno]chrysene-6,12-dione	C22H8Br2O2	10 - 100	C.I. 59300 C.I. Pigment Red 168								X
207-586-9	482-89-3	2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-3H-indol-3-one	C11H12O3	1,000 - 10,000	C.I. 73000 ;C.I. Pigment Blue 66	X	X						X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
226-866-1	5521-31-3	2,9-dimethylanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone	C30H58O7S. Na	100 - 1,000	C.I. 71130 C.I. Pigment Red 179	X	X	X					X
402-400-4	54660-00-3	3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione	-	10 - 100	C.I. 561050 C.I. Pigment Red 255	X	X	X	X				X
403-530-4	129423-54-7	calcium 4-chloro-2-(5-hydroxy-3-methyl-1-(3-sulfonatophenyl)pyrazol-4-ylazo)-5-methylbenzenesulfonate	-	10 - 100	C.I. 18795 C.I. Pigment Yellow 191	X		X	X				X
404-110-3	-	Pigmentadditiv RL	-	Tonnage Data Confidential	-								
410-210-8	-	Pigment Red 5021B	-	1-10	-								
410-510-9	-	Yellow pigment additive	-	1-10	-								
411-080-5	-	Pigment Yellow FC 26290	-	10 - 100	-								X
413-920-6	88949-33-1	3,6-bis-biphenyl-4-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione	-	1-10	C.I. 561300 C.I. Pigment Red 264	X			X				X
419-370-3	-	PIGMENT RED 3092C	-	Tonnage Data Confidential	-								
431-150-9	-	Lexmark Black Pigment	-	Tonnage Data Confidential	-								
460-020-4	-	PIGMENT ROT 5021 A	-	Tonnage Data Confidential	-								
616-466-9	77501-63-4	(2-ethoxy-1-methyl-2-oxoethyl)-5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate	-	Tonnage Data Confidential	-								X

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
416-250-2	84632-59-7	2-cyano-N-(2,4-dichloro-5-methoxyphenyl)acetamide		20 - 120+	C.I. 561170 C.I. Pigment Orange 73	X			X				
909-082-0	938065-79-3	Reaction mass of 5,12-dihydro-2,9-dimethylquino[2,3-b]acridine-7,14-dione and 5,12-dihydro-2-methylquino[2,3-b]acridine-7,14-dione and 5,12-dihydroquino[2,3-b]acridine-7,14-dione	-	10 - 100	C.I. Pigment Red 282	X	X	X					
910-670-4	Multi constituent substance	Falu Rödfärg Pigment	-	100 - 1,000	-	X							
911-436-4	Multi constituent substance	Reaction mass of 4-[[4-(aminocarbonyl)phenyl]azo]-N-(2-ethoxyphenyl)-3-hydroxynaphthalene-2-carboxamide and 4-[[4-(aminocarbonyl)phenyl]azo]-3-hydroxy-N-(2-methoxyphenyl)naphthalene-2-carboxamide	-	10 - 100	-								
911-715-0	Multi constituent substance	Reaction mass of 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(2,1-diazenediyl)]bis[N-(2,4-dimethylphenyl)-3-oxobutyramide] and 2-[2-[3,3'-dichloro-4'-[2-[1-[[(2,4-dimethylphenyl)amino]carbonyl]-2-oxopropyl]diazenyl][1,1'-biphenyl]-4-yl]diazenyl]-3-oxo-N-(o-tolyl)butyramide and 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(2,1-diazenediyl)]bis[N-(2-methylphenyl)-3-oxobutyramide]	-	1,000 - 10,000	Pigment Yellow 174		X						

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
939-379-0		nickel, 5,5'-azobis-2,4,6(1H,3H,5H)-pyrimidinetrione complexes and melamine	C3H6N6	100 - 1,000	-	X	X						
Pigments to be registered by 2018 by the Inorganic Pigment Consortium													
234-443-8	12003-86-0	Aluminium yttrium trioxide	AlO3Y	reg 2018	C.I.77788			X			X		
234-637-2	12018-19-8	Dichromium zinc tetraoxide	Cr2O4Zn	reg 2018	-						X		
235-107-3	12068-86-9	Diiron magnesium tetraoxide	(Fe, Mg)O	reg 2018	-								
236-655-6	13455-36-2	tricobalt bis(orthophosphate)	-	reg 2018	-								
269-055-8	68186-93-6	Tin vanadium yellow cassiterite	(Sn.V)O2	reg 2018	C.I.77862						X		
269-058-4	68186-96-9	Spinels, chromium iron manganese zinc brown	(Zn,Fe,Mn)(Fe,Cr,Mn)O4	reg 2018	-						X	X	
269-062-6	68187-00-8	Titanium vanadium antimony grey rutile	-	reg 2018	-								
269-064-7	68187-02-0	Spinels, iron titanium brown	-	reg 2018	-	X		X			X		
269-066-8	68187-05-3	Spinels, cobalt tin grey	Co2SnO4	reg 2018	-	X		X					
269-069-4	68187-09-7	Iron chromite brown spinel	Fe(Fe,Cr)2O4	reg 2018	C.I.77501	X		X			X	X	
269-083-0	68187-27-9	Chrome alumina pink corundum	-	reg 2018	-								
269-101-7	68187-49-5	Cobalt chromite green spinel	CoCr2O4	reg 2018	C.I.77344	X		X			X	X	
269-102-2	68187-50-8	Iron cobalt black spinel	(Fe,Co)Fe2O4	reg 2018	C.I. 77498.								
269-104-3	68187-53-1	Chrome tin orchid cassiterite	(Sn,Cr)O2	reg 2018	C.I.77863						X		
269-105-9	68187-54-2	Tin antimony grey cassiterite	(Sn,Sb)O2	reg 2018	C.I.77865			X			X	X	

EC Number	CAS Number	Name (as indicated in the registration)	Generic formula	Registered tonnage , t/y	Colour Index number	Uses as indicated in the registrations or by the IP Consortium							
						Paints	Inks	Plastics	Finger paint	Adhesives	Ceramics	Construction	Other
269-230-9	68201-65-0	Chrome alumina pink spinel	-	reg 2018	-								
270-208-6	68412-74-8	Cobalt zinc silicate blue phenacite	$(Co,Zn)_2SiO_4$	reg 2018	C.I.77366	X		X			X		
271-385-2	68553-01-5	Victoria green garnet	3CaOáCr2O3á3SiO2	reg 2018	C.I.77300						X		
271-891-3	68611-42-7	Chrome niobium titanium buff rutile	-	reg 2018	-								
271-892-9	68611-43-8	Nickel niobium titanium buff rutile	-	reg 2018	-								
277-135-9	72968-34-4	Zircon, cadmium yellow	CdS in $ZrSiO_4$	reg 2018	-						X		
305-837-8	95046-49-4	Spinels, copper green	CuO on SiO_2	reg 2018	-						X		
305-908-3	95193-93-4	Rutiles, antimony titanium yellow orange	-	reg 2018	-								
306-013-0	95465-97-7	Spinels, chromium green	-	reg 2018	-						X		
310-073-3	102110-71-4	Aluminium oxide	(Al_2O_3), solid soln. with iron oxide (Fe_2O_3)	reg 2018	-			X			X		

Appendix 3: Pigments registered in the Danish Productregister

CAS No	EC No	Name *1	n, *3 products	n, , *3 companies	Consumption, t/y mean value *2	REACH registered tonnage, t/y
Inorganic pigments						
1308-38-9	215-160-9	Chromium (III) oxide	105	37	183.0	10,000 - 100,000
1309-37-1	215-168-2	Diiron trioxide	996	145	4056.3	100,000 - 1,000,000
1314-13-2	215-222-5	Zinc oxide	563	111	709.6	100,000 - 1,000,000
1314-41-6	215-235-6	Orange lead	..	..	..	10,000 - 100,000
1314-98-3	215-251-3	Zinc sulphide	24	14	5.6	100,000 - 1,000,000
1317-36-8	215-267-0	Lead monoxide	45	12	142.0	100,000 - 1,000,000
1317-60-8	215-275-4	Hematite (Fe2O3)	64	14	46.6	10,000 - 100,000
1317-61-9	215-277-5	Triiron tetraoxide	341	90	240.2	100,000 - 1,000,000
1317-80-2	215-282-2	Rutile (TiO2)	119	48	300.5	10,000 - 100,000
1333-86-4	215-609-9	Carbon black	1448	190	251.1	1,100,000 - 11,000,000
1345-16-0	310-193-6	Cobalt aluminate blue spinel	25	10	6.5	1,000 - 10,000
8007-18-9	232-353-3	Antimony nickel titanium oxide yellow	23	13	36.0	1,000 - 10,000
10101-66-3	233-257-4	Ammonium manganese(3+) diphosphate	..	..	..	10 - 100
12656-85-8	235-759-9	Lead chromate molybdate sulfate red	33	16	16.5	1,000 - 10,000
12737-27-8	235-790-8	Chromium iron oxide	..	..	..	10,000 - 100,000
12062-81-6	235-049-9	Iron manganese trioxide	24	9	3.8	1,000 - 10,000
51274-00-1	257-098-5	iron hydroxide oxide yellow	472	72	228.0	100,000 - 1,000,000
13463-67-7	236-675-5	Titanium dioxide	2691	256	21405.0	1,000,000-10,000,000
14059-33-7	237-898-0	Bismuth vanadium tetraoxide	92	24	8.1	1,000 - 10,000
68186-85-6	269-047-4	Cobalt titanite green spinel	4	3	1.6	10 - 100
68186-87-8	269-049-5	Cobalt zinc aluminate blue spinel	..	..	..	100 - 1,000
68186-90-3	269-052-1	Chrome antimony titanium buff rutile	63	20	10.7	10,000 - 100,000
68186-91-4	269-053-7	Copper chromite black spinel	21	8	2.8	1,000+
68186-94-7	269-056-3	Manganese ferrite black spinel	26	11	3.2	1,000 - 10,000
68187-11-1	269-072-0	Cobalt chromite blue green spinel	..	..	..	100 - 1,000
58339-34-7	261-218-1	Cadmium sulfoselenide red	..	..	..	100 - 1,000
68187-40-6	269-093-5	Olivine, cobalt silicate blue	..	..	..	1,000 - 10,000
68187-49-5	269-101-7	Cobalt chromite green spinel	..	..	..	Reg 2018
68187-51-9	269-103-8	Zinc ferrite brown spinel	..	..	..	1,000 - 10,000
68187-54-2	269-105-9	Tin antimony grey cassiterite	..	..	..	Reg 2018
68412-74-8	270-208-6	Cobalt zinc silicate blue phenacite	..	..	..	Reg 2018
101357-30-6	309-928-3 (same as below)	Silicic acid, aluminum sodium salt, sulfurized	6	6	21.0	n.r.
57455-37-5	309-928-3	Silicic acid, aluminum sodium salt, sulfurized	35	17	119.0	10,000 - 100,000

CAS No	EC No	Name *1	n, *3 prod-ucts	n, , *3 compa-nies	Consumption, t/y mean value *2	REACH registered tonnage, t/y
102184-95-2	310-077-5	Silicic acid, zirconium salt, cadmium pigment-encapsulated	..	..	..	100 - 1,000
Organic pigments						
147-14-8	205-685-1	C.I. Pigment Blue 15	516	102	57.2	10,000 - 100,000
980-26-7	213-561-3	C.I. Pigment Red 122	98	30	16.9	1,000 - 10,000
1047-16-1	213-879-2	C.I. Pigment Violet 19	153	39	14.9	1,000 - 10,000
1103-38-4	214-160-6	C.I. Pigment Red 49, barium salt (2:1)	..	..	..	1 - 10
1324-76-1	215-385-2	C.I. Pigment Blue 61	..	..	..	n.r.
1325-75-3	215-406-5	C.I. Pigment Green 1	..	..	..	n.r.
1325-82-2	603-635-7	C.I. Pigment Violet 3	3	3	0.0	n.r.
1326-03-0	215-413-3	C.I. Pigment Violet 1	..	..	..	n.r.
1326-04-1	215-414-9	C.I. Pigment Violet 2	..	..	..	n.r.
1328-53-6	215-524-7	C.I. Pigment Green 7	281	72	44.4	1,000 - 10,000
1503-48-6	216-125-0	Quino(2,3-b)acridine-6,7,13,14(5h,12h)-tetrone	..	..	..	n.r.
2379-74-0	219-163-6	C.I. Pigment Red 181	..	..	..	n.r.
2387-03-3	219-210-0	C.I. Pigment Yellow 101	..	..	..	n.r.
2425-85-6	219-372-2	C.I. Pigment Red 3	28	14	5.4	10 - 100
2512-29-0	219-730-8	C.I. Pigment Yellow 1	7	7	0.3	100 - 1,000
2786-76-7	220-509-3	C.I. Pigment Red 170	144	36	18.5	100 - 1,000
2814-77-9	220-562-2	C.I. Pigment Red 4	6	4	0.1	100 - 1,000
3049-71-6	221-264-5	C.I. Pigment Red 178	..	..	..	100 - 1,000
3089-17-6	221-424-4	C.I. Pigment Red 202	22	10	2.8	100 - 1,000
3468-63-1	222-429-4	C.I. Pigment Orange 5	36	12	5.6	100 - 1,000
3520-72-7	222-530-3	C.I. Pigment Orange 13	8	7	36.0	100 - 1,000
3564-22-5	222-643-8	C.I. Pigment Red 18	..	..	..	n.r.
3905-19-9	223-460-6	C.I. Pigment Red 166	9	5	2.9	100 - 1,000
4051-63-2	223-754-4	C.I. Pigment Red 177	15	7	2.0	100 - 1,000
4216-01-7	224-151-9	C.I. Pigment Yellow 108	3	3	0.1	n.r.
4216-02-8	224-152-4	C.I. Pigment Red 194	..	..	..	n.r.
4378-61-4	224-481-3	C.I. Pigment Red 168	17	10	1.1	10 - 100
4424-06-0	224-597-4	C.I. Pigment Orange 43	17	9	0.4	n.r.
4531-49-1	224-867-1	C.I. Pigment Yellow 17	6	3	12.1	100 - 1,000
4948-15-6	225-590-9	C.I. Pigment Red 149	..	..	..	100 - 1,000
5045-40-9	225-744-5	C.I. Pigment Yellow 109	7	3	0.5	n.r.
5102-83-0	225-822-9	C.I. Pigment Yellow 13	34	13	12.5	1,000 - 10,000
5160-02-1	225-935-3	C.I. Pigment Red 53, barium salt (2:1)	16	5	9.8	1,000 - 10,000
5280-66-0	226-102-7	C.I. Pigment Red 48, manganese(2+) salt	17	7	2.0	10 - 100
5280-68-2	226-103-2	C.I. Pigment Red 146	21	10	1.6	100 - 1,000
5280-80-8	226-107-4	C.I. Pigment Yellow 95	..	..	..	100 - 1,000
5281-04-9	226-109-5	C.I. Pigment Red 57:1	21	6	19.0	10,000 - 100,000
5468-75-7	226-789-3	C.I. Pigment Yellow 14	8	6	1.1	1,000 - 10,000
5521-31-3	226-866-1	C.I. Pigment Red 179	27	9	4.6	100 - 1,000
5567-15-7	226-939-8	C.I. Pigment Yellow 83	125	27	19.6	1,000 - 10,000

CAS No	EC No	Name *1	n, *3 prod-ucts	n, , *3 compa-nies	Consumption, t/y mean value *2	REACH registered tonnage, t/y
5580-57-4	226-970-7	C.I. Pigment Yellow 93	..	..	..	100 - 1,000
5590-18-1	226-999-5	Pigment Yellow 110	30	13	6.0	n.r.
5979-28-2	227-783-3	C.I. Pigment Yellow 16	7	3	0.2	n.r.
6041-94-7	227-930-1	C.I. Pigment Red 2	23	6	4.3	1,000 - 10,000
6358-30-1	613-252-7	C.I. Pigment Violet 023	251	49	36.0	1,000 - 10,000
6358-31-2	228-768-4	C.I. Pigment Yellow 74	168	43	30.3	1,000 - 10,000
6358-37-8	228-771-0	C.I. Pigment Yellow 55	..	..	..	1 - 10
6358-85-6	228-787-8	C.I. Pigment Yellow 12	26	11	0.1	10,000 - 100,000
6358-87-8	228-788-3	C.I. Pigment Red 38	..	..	..	10 - 100
6372-81-2	228-906-3	Barium bis[2-[(2-hydroxy-1-naphthyl)azo]benzoate]	..	..	..	n.r.
6407-75-6	229-040-9	4-[(2,5-Dichlorophenyl)azo]-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one	..	..	..	n.r.
6410-26-0	229-096-4	C.I. Pigment Red 21	..	..	..	n.r.
6410-32-8	229-102-5	C.I. Pigment Red 12	..	..	..	10 - 100
6410-41-9	229-107-2	C.I. Pigment Red 5	..	..	..	10 - 100
6448-95-9	229-245-3	C.I. Pigment Red 22	..	..	..	1 - 10
6471-49-4	229-313-2	C.I. Pigment Red 23	..	..	..	n.r.
6486-23-3	229-355-1	C.I. Pigment Yellow 3	8	7	4.1	100 - 1,000
6528-34-3	229-419-9	C.I. Pigment Yellow 65	3	3	0.0	100 - 1,000
6535-46-2	229-440-3	C.I. Pigment Red 112	85	26	18.5	1,000 - 10,000
6985-92-8	230-249-2	C.I. Pigment Red 175	..	..	..	n.r.
6992-11-6	230-258-1	C.I. Pigment Brown 25	10	7	3.6	10 - 100
7023-61-2	230-303-5	C.I. Pigment Red 48, calcium salt (1:1)	7	4	1.5	1,000 - 10,000
7585-41-3	231-494-8	C.I. Pigment Red 48, barium salt (1:1)	3	3	0.2	100 - 1,000
10142-77-5	600-210-8	C.I. pigment red 117	..	..	..	n.r.
12224-98-5	235-424-7	C.I. Pigment Red 81	..	..	..	n.r.
12225-08-0	235-426-8	C.I. Pigment Violet 32	..	..	..	10 - 100
12225-18-2	235-427-3	C.I. Pigment Yellow 97	28	8	0.6	100 - 1,000
12236-62-3	235-462-4	C.I. Pigment Orange 36	102	24	17.7	100 - 1,000
12237-62-6	235-468-7	C.I. Pigment Violet 27	..	..	..	100 - 1,000
12238-31-2	235-471-3	C.I. Pigment Red 52:2	9	4	0.1	1 - 10
12239-87-1	235-476-0	Copper chlorophthalocyanine	20	9	0.4	1,000 - 10,000
12240-15-2	602-780-3	C.I. Pigment Blue 27	..	..	..	n.r.
12286-65-6	235-557-0	C.I. Pigment Yellow 61	..	..	..	10 - 100
12768-99-9	603-227-9	C.I. Pigment Orange 42	..	..	..	n.r.
13515-40-7	236-852-7	C.I. Pigment Yellow 73	25	5	0.1	100 - 1,000
14154-42-8	237-998-4	Chloro[29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]aluminium	..	..	..	n.r.
14295-43-3	238-222-7	C.I. Pigment Red 88	..	..	..	n.r.
14302-13-7	238-238-4	C.I. Pigment Green 36	124	27	12.2	100 - 1,000
14569-54-1	238-611-1	C.I. Pigment Yellow 63	..	..	..	n.r.
15680-42-9	239-763-1	C.I Pigment Yellow 129	13	6	0.7	n.r.

CAS No	EC No	Name *1	n, *3 prod-ucts	n, , *3 compa-nies	Consumption, t/y mean value *2	REACH registered tonnage, t/y
15782-05-5	239-879-2	C.I. Pigment Red 48, strontium salt (1:1)	5	3	2.8	100 - 1,000
15790-07-5	239-888-1	C.I. Pigment Yellow 104	..	..	..	1-10
15793-73-4	239-898-6	C.I. Pigment Orange 34	76	25	21.8	100 - 1,000
15993-42-7	240-131-2	N-(5-chloro-2-methoxyphenyl)-2-[(2-methoxy-4-nitrophenyl)azo]-3-oxobutyramide	..	..	..	10 - 100
16043-40-6	605-208-0	Quino[2,3-b]acridine-7,14-dione, 5,12-dihydro-3,10-dimethyl-	4	3	0.2	n.r.
16521-38-3	240-589-3	C.I. Pigment Blue 63	..	..	..	n.r.
17832-28-9	241-793-5	1-Butanol, 4-(ethenyloxy)-	..	..	..	Confidential
22094-93-5	244-776-0	C.I. Pigment Yellow 81	7	3	0.5	10 - 100
27614-71-7	248-573-8	Copper, (tetrachloro-29h,31h-phthalocyaninato(2-)-n29,n30,n31,n32)-	..	..	..	100 - 1,000
29204-84-0	249-503-9	Nickel, bis(2,3-bis(hydroxyimino)-n-phenylbutanamidato-n2,n3)-	6	3	0.7	n.r.
29920-31-8	249-955-7	C.I. Pigment Yellow 120	..	..	..	10 - 100
30125-47-4	250-063-5	C.I Pigment Yellow 138	42	13	13.6	100 - 1,000
31775-16-3	250-797-6	2,2'-[(3,3'-Dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(4-methoxyphenyl)-3-oxobutyramide]	19	4	1.1	n.r.
31778-10-6	250-800-0	C.I Pigment Red 208	..	..	..	10 - 100
31837-42-0	250-830-4	C.I. Pigment Yellow 151	58	12	5.6	100 - 1,000
35355-77-2	252-525-1	C.I. Pigment Red 63:2	..	..	..	
35636-63-6	252-650-1	C.I Pigment Yellow 175	..	..	..	10 - 100
36888-99-0	253-256-2	C.I Pigment Yellow 139	65	21	19.6	1,000-10,000
36968-27-1	253-292-9	C.I Pigment Red 266	..	..	..	1-10
37300-23-5	609-398-6	C.I. Pigment Yellow 36	..	..	..	n.r.
42844-93-9	255-965-2	[1,3-dihydro-5,6-bis[[(2-hydroxy-1-naphthyl)methylene]amino]-2H-benzimidazol-2-onato(2-)-N5,N6,O5,O6]nickel	..	..	..	n.r.
52846-56-7	258-221-5	C.I Pigment Orange 62	..	..	..	10 - 100
54660-00-3	611-183-7	C.I. Pigment Red 255	21	8	3.3	10 - 100
59487-23-9	261-785-5	C.I. Pigment Red 187	13	3	0.3	10 - 100
61512-61-6	612-162-5	C.I. Pigment Orange 51	..	..	..	n.r.
61847-48-1	263-272-1	C.I. Pigment Red 188	20	6	0.9	100 - 1,000
61951-98-2	263-353-1	C.I. Pigment Red 185	..	..	..	n.r.
65212-77-3	265-634-4	C.I Pigment Yellow 183	..	..	..	100 - 1,000
67989-22-4	268-006-8	C.I. Basic Violet 1, molybdatephosphate	..	..	..	n.r.
68134-22-5	268-734-6	C.I Pigment Yellow 154	20	8	13.0	100 - 1,000

CAS No	EC No	Name *1	n, *3 prod-ucts	n, , *3 compa-nies	Consumption, t/y mean value *2	REACH registered tonnage, t/y
68227-78-1	269-389-4	C.I. Pigment Red 147	..	..	..	1 - 10
68511-62-6	270-944-8	Pigment Yellow 150	10	8	0.8	n.r.
68512-13-0	270-958-4	C.I. Pigment Green 36	25	7	1.1	100 - 1,000
68516-73-4	271-176-6	C.I Pigment Yellow 155	12	3	1.0	100 - 1,000
68610-86-6	271-878-2	C.I. Pigment Yellow 127	..	..	..	100 - 1,000
68987-63-3	273-501-7	C.I. Pigment Blue 76	6	3	0.6	1,000 - 10,000
71832-85-4	276-057-2	C.I Pigment Yellow 168	..	..	..	10 - 100
71872-63-4	615-664-2	C.I. Pigment Red 222	..	..	..	n.r.
72102-84-2	276-344-2	C.I. Pigment Orange 64	..	..	..	n.r.
72639-39-5	276-755-7	Nitrophenyl 3-[[2-hydroxy-3-[(2-methylphenyl)carbamoyl]-1-naphthyl]azo]-4-methoxybenzenesulphonate	14	3	0.3	n.r.
74336-59-7	277-823-9	C.I Pigment Orange 67	31	9	1.8	100 - 1,000
74336-60-0	277-824-4	1-[(5,7-Dichloro-1,9-dihydro-2-methyl-9-oxopyrazolo[5,1-b]quinazolin-3-yl)azo]anthraquinone	..	..	..	n.r.
74441-05-7	277-873-1	C.I Pigment Yellow 181	..	..	..	100 - 1,000
77804-81-0	278-770-4	C.I Pigment Yellow 180	..	..	..	100 - 1,000
78521-39-8	278-934-5	6-[[(4-Methylphenyl)sulphonyl]amino]hexanoic acid	..	..	..	100 - 1,000
78952-72-4	279-017-2	2-[[3,3'-Dichloro-4'-[[1-[[(2,4-dime-thylphenyl)amino]carbonyl]-2-oxopropyl]azo][1,1'-biphenyl]-4-yl]azo]-3-oxo-N-(o-tolyl)butyramide	..	..	..	n.r.
79953-85-8	279-356-6	C.I Pigment Yellow 128	..	..	..	100 - 1,000
82199-12-0	279-914-9	C.I Pigment Yellow 194	16	7	0.6	100 - 1,000
83524-75-8	280-472-4	2,9-bis(p-methoxybenzyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone	..	..	..	n.r.
84632-50-8	617-600-9	Benzonitrile, 3,3'-(2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl)bis-	..	..	..	n.r.
84632-59-7	617-601-4	C.I. Pigment Orange 73	9	6	0.7	20 - 120+
84632-65-5	617-603-5	C.I. Pigment Red 254	84	26	17.5	10-100
84632-66-6	617-604-0	2,5-Dihydro-3,6-bis(4-methylphenyl)-pyrrolo[3,4-c]pyrrole-1,4-dione				n.r.
85776-13-2	N/A	C.I. Pigment Red 253	8	3	0.1	n.r.

CAS No	EC No	Name *1	n, *3 prod-ucts	n, , *3 compa-nies	Consumption, t/y mean value *2	REACH registered tonnage, t/y
85776-14-3	N/A	2-Naphthalenecarboxamide, n-(4-chlorophenyl)-4-((2,5-dichloro-4-((dimethyla-mino)sulfonyl)phenyl)azo)-3-hydroxy-	..	..	..	n.r.
85958-80-1	288-967-7	[[3-[1-Cyano-2-(methylamino)-2-oxoethylidene]-2,3-dihydro-1H-isoindol-1-yli-dene](salicylic)hydrazidato(2-)]nickel	..	..	..	n.r.
85959-60-0	289-055-1	C.I. Pigment Orange 69	..	..	..	n.r.
88949-33-1	618-223-2	C.I. Pigment Red 264	9	6	0.4	1-10
90268-23-8	290-823-3	C.I. Pigment Yellow 126	..	..	..	10 - 100
99402-80-9	619-430-0	C.I. Pigment Red 184	6	4	0.4	10 - 100
106276-80-6	600-736-8	C.I Pigment Yellow 110	..	..	..	100 - 1,000
215247-95-3	606-790-9	Diindolo[2,3-c:2',3'-n]triphenodioxazine, 9,19-dichloro-5,15-diethyl-5,15-dihydro-	..	..	..	n.r.
		Total	6,281	589	28,461	2,800,000-28,000,000

.. Data are confidential

*1 For inorganic pigments the preregistering name is indicated, because the name indicated the composition of the pigment. For organic pigments, the name registered in the Productregister is indicated because the C.I. pigment names are the names usually used to identify the pigments.

*2 Registered consumption = registered manufacture/import - export (average figures).

*3 Number of registered products and number of companies, which have notified products with the pigment.

Appendix 4: Pigments in paints and varnishes registered in the Danish Productregister

Data from the Danish Productregister on pigments used in paint for non-industrial applications are shown in the table below. The table exclude application areas (UC62 categories) where it is explicitly indicated that the paint and varnishes are for industrial applications. The table shows total consumption for 46 pigments with non-confidential data for the application areas concerned. The listed pigments account for 94% of the total consumption of all pigments in the product categories concerned.

The table include the average minimum and maximum concentrations registered for a specific product. It should be noted that the pigments are often used in combination, which explain the low minimum values.

CAS No	Pigment name	Consumption, t/y	Min konc, %	Max konc, %
13463-67-7	Titanium dioxide	1125.5	0.01	35.00
1309-37-1	Diiron trioxide	216.6	<0.00	41.00
1317-61-9	Triiron tetraoxide	82.2	0.24	1.38
1333-86-4	Carbon black	72.0	2.98	61.33
1308-38-9	Chromium (III) oxide	57.5	0.01	20.57
1314-13-2	Zinc oxide	41.4	<0.00	80.00
3520-72-7	C.I. Pigment Orange 13	36.0	<0.00	35.58
51274-00-1	Iron hydroxide oxide yellow	33.1	<0.00	80.00
1317-80-2	Rutile (TiO2)	17.1	1.04	25.70
147-14-8	C.I. Pigment Blue 15	11.1	<0.00	31.01
1328-53-6	C.I. Pigment Green 7	9.1	<0.00	80.00
1047-16-1	C.I. Pigment Violet 19	7.5	<0.00	85.08
12236-62-3	C.I. Pigment Orange 36	6.7	0.25	47.90
84632-65-5	C.I. Pigment Red 254	5.9	<0.00	35.00
5567-15-7	C.I. Pigment Yellow 83	5.7	<0.00	35.00
6535-46-2	C.I. Pigment Red 112	5.7	1.15	25.00
14059-33-7	Bismuth vanadium tetraoxide	5.4	<0.00	15.00
6358-31-2	C.I. Pigment Yellow 74	5.2	2.35	10.00
6358-30-1	C.I. Pigment Violet 023	4.9	0.12	35.00
14302-13-7	C.I. Pigment Green 36	4.8	0.05	45.00
31837-42-0	C.I. Pigment Yellow 151	4.4	0.26	20.50
36888-99-0	C.I Pigment Yellow 139	4.3	0.01	32.00
2786-76-7	C.I. Pigment Red 170	4.1	0.10	18.00
5590-18-1	Pigment Yellow 110	3.5	0.02	80.00
68134-22-5	C.I Pigment Yellow 154	3.3	0.19	33.61
68186-90-3	Chrome antimony titanium buff rutile	3.3	0.09	32.00
980-26-7	C.I. Pigment Red 122	2.9	0.10	61.33
54660-00-3	C.I. Pigment Red 255	2.5	0.01	55.00

CAS No	Pigment name	Consump-tion, t/y	Min konc, %	Max konc, %
30125-47-4	C.I Pigment Yellow 138	2.4	0.44	18.11
3089-17-6	C.I. Pigment Red 202	2.2	<0.00	3.78
5521-31-3	C.I. Pigment Red 179	2.2	1.49	25.00
4378-61-4	C.I. Pigment Red 168	2.1	<0.00	33.88
4051-63-2	C.I. Pigment Red 177	1.9	1.93	30.00
15793-73-4	C.I. Pigment Orange 34	1.2	<0.00	32.00
2425-85-6	C.I. Pigment Red 3	1.0	0.98	18.89
5280-66-0	C.I. Pigment Red 48, manganese(2+) salt	0.7	0.01	0.27
8007-18-9	Antimony nickel titanium oxide yellow	0.7	<0.00	33.40
12656-85-8	Lead chromate molybdate sulfate red	0.6	0.02	30.00
68987-63-3	C.I. Pigment Blue 76	0.6	0.10	38.50
15680-42-9	C.I Pigment Yellow 129	0.5	0.12	15.00
88949-33-1	C.I. Pigment Red 264	0.5	1.19	4.84
68512-13-0	C.I. Pigment Green 36	0.5	1.27	8.50
6992-11-6	C.I. Pigment Brown 25	0.4	0.14	31.00
3468-63-1	C.I. Pigment Orange 5	0.4	<0.00	33.00
12239-87-1	Copper chlorophthalocyanine	0.1	1.51	6.26
6358-85-6	C.I. Pigment Yellow 12	0.0	<0.00	20.50
Total listed		1799.6		

Appendix 5: Pigments in printing inks registered in the Danish Productregister

Data from the Danish Productregister on pigments used in pinting inks (UC 62 code 45, reprographic agents) are shown in Appendix 3. The table shows total consumption for 41 pigments with non-confidential data for the application areas concerned. The listed pigments account for 93% of the total consumption of all pigments in the product categories concerned.

The table include the average minimum and maximum concentrations registered for a specific product. It should be noted that the pigments are often used in combination, which explain the low minimum values.

CAS No	Pigment name	Consumption, t/y	Min konc, %	Max konc, %
13463-67-7	Titanium dioxide	227.0	0.3	68.0
1333-86-4	Carbon black	28.6	0.0	42.5
147-14-8	C.I. Pigment Blue 15	26.7	0.0	40.0
1328-53-6	C.I. Pigment Green 7	23.9	0.1	37.8
6358-30-1	C.I. Pigment Violet 023	19.6	0.1	39.2
5281-04-9	C.I. Pigment Red 57:1	19.0	0.8	24.9
15793-73-4	C.I. Pigment Orange 34	16.4	0.2	21.0
6358-31-2	C.I. Pigment Yellow 74	10.4	0.0	38.5
1309-37-1	Diiron trioxide	10.3	0.0	62.5
5160-02-1	C.I. Pigment Red 53, barium salt (2:1)	9.8	1.0	35.4
51274-00-1	Iron hydroxide oxide yellow	6.8	3.0	55.0
980-26-7	C.I. Pigment Red 122	5.5	1.2	40.0
6041-94-7	C.I. Pigment Red 2	4.3	12.0	29.3
5102-83-0	C.I. Pigment Yellow 13	3.9	2.3	19.2
3905-19-9	C.I. Pigment Red 166	2.9	0.1	20.0
6535-46-2	C.I. Pigment Red 112	2.7	6.6	30.0
30125-47-4	C.I Pigment Yellow 138	1.7	2.0	38.0
74336-59-7	C.I Pigment Orange 67	1.4	5.6	18.7
5468-75-7	C.I. Pigment Yellow 14	1.1	1.3	33.0
14302-13-7	C.I. Pigment Green 36	1.0	5.0	40.0
1317-61-9	Triiron tetraoxide	1.0	4.7	29.5
5567-15-7	C.I. Pigment Yellow 83	0.9	0.3	40.0
7023-61-2	C.I. Pigment Red 48, calcium salt (1:1)	0.9	6.6	27.0
1047-16-1	C.I. Pigment Violet 19	0.8	0.0	15.3
36888-99-0	C.I Pigment Yellow 139	0.7	0.2	35.5
84632-65-5	C.I. Pigment Red 254	0.7	0.0	37.5
12236-62-3	C.I. Pigment Orange 36	0.7	0.6	37.5
2786-76-7	C.I. Pigment Red 170	0.7	2.3	29.3
22094-93-5	C.I. Pigment Yellow 81	0.5	4.6	40.0
5280-68-2	C.I. Pigment Red 146	0.5	0.4	40.0

CAS No	Pigment name	Consumption, t/y	Min konc, %	Max konc, %
14059-33-7	Bismuth vanadium tetraoxide	0.5	11.0	59.0
4424-06-0	C.I. Pigment Orange 43	0.3	0.4	17.0
82199-12-0	C.I Pigment Yellow 194	0.3	3.2	13.8
1317-80-2	Rutile (TiO2)	0.2	9.0	13.0
5590-18-1	Pigment Yellow 110	0.2	4.2	13.7
7585-41-3	C.I. Pigment Red 48, barium salt (1:1)	0.2	7.1	40.0
12225-18-2	C.I. Pigment Yellow 97	0.1	1.9	9.8
3089-17-6	C.I. Pigment Red 202	0.1	1.4	5.4
6358-85-6	C.I. Pigment Yellow 12	0.1	0.0	2.3
4051-63-2	C.I. Pigment Red 177	0.1	1.7	9.0
68511-62-6	Pigment Yellow 150	0.02	1.6	2.9
Total listed		430		

Appendix 6: Pigments in selected products not specifically exempt from the Danish Nanoproduct Register

The following Appendix presents information on pigments in selected products on the Danish market not specifically exempt from the Danish Nanoproduct Register as taken from a number of Danish EPA consumer project reports and non-confidential information (at least three products and notifiers per pigment/application) from the Danish Productregister.

A6,1 Cleaning agents

Pigments registered in the Danish Productregister for "cleaning/washing" agents are shown in the table below. The majority of cleaning and washing agents used by both professionals (and consumers) are probably not registered in the Productregister because they do not include substances with a harmonised classification. For the registered mixtures, titanium dioxide accounts for nearly 100%. Titanium dioxide is registered for "general cleaning agents", "washing agents" and "dishwashing agents".

Products for consumers include pigmented washing agents for washing of white-pigmented wood floors. These products, not registered in the Productregister, most likely contain titanium dioxide as the white pigment.

TABLE 27
PIGMENTS WITH NON-CONFIDENTIAL CONSUMPTION IN CLEANING/WASHING AGENTS REGISTERED IN THE PRODUCTREGISTER

CAS No	Chemical name	Number of products	Number of notifiers	Registered consumption, average t/y *1	% of total
13463-67-7	Titanium dioxide	102	21	12.62	99.4%
1314-13-2	Zinc oxide			0.06	0.4%
147-14-8	C.I. Pigment Blue 15	6	6	0.01	0.1%
1309-37-1	Diiron trioxide	5	3	0.00	0.0%
	Other (5 confidential)			0.01	0.1%
Total incl. confidential				**12.69**	**100%**

*1 Registered consumption = content of registered products. Consumption = production/import - export. According to UC62 Codes.

A6,2 Printing inks for textile printing and textile colourants for home use

Textile dyes can be divided into decoration dyes and products for textile dying, of which 80% of the total consumption is composed of the latter. The group of decoration dyes includes products such as felt-tip pens, pop-up dyes, and transfer dyes. The group of products for textile dying includes textile paint intended for dying or covering textiles in larger proportions. A Danish consumer product project on substances in textile colorants estimated the annual Danish consumption of these types of colours to approximately 30 t/y (Egmose and Pors, 2005). 42 products were identified in this study and 15 of these were taken out for elemental screening analysis. Copper, antimony and one product with lead were identified, which likely result from pigments, but the analyses did not identify individual pigments. Five products were subject to azo-dye analysis and as no aromatic amines were detected it is concluded that this could indicate that the products did not contain any prohibited azo dyes.

In a Danish EPA project on fluorescent substances in consumer products, Pedersen et al. (2003) looked at 24 different products. Of possible relevance for the Danish Nanoproduct register, Zinc Sulphide (CAS-no 1314-98-3) was declared as a pigment in Textile colorants.

Pigments in inks for textile printing and textile colorants for home use cannot be extracted from the Productregister.

A6,3 Printing inks and toners for consumer use (e.g. cartridges for inkjet printers or laser printers used by consumers)

Data for toners and other chemicals for photocopiers/laser printers in the Productregister are confidential as the number of products or notifiers are less than three for each pigment. No data are available from the Danish EPA's consumer product projects.

A6,4 Candles (if nanosized pigments are released as such during use)

No data on pigments in candles are available from the Productregister or from the Danish EPAss consumer product projects.

A6,5 Maintenance agents

Maintenance agents, which may contain pigments, include:

- Shoe care products and other products for colouring leather
- Floor wax
- Metal polish
- Car maintenance products (various products)
- Undercarriage maintenance products (for cars).

Shoe care products and other products for colouring leather - Data on pigments in shoe care products and other products for colouring of leather in the Productregister are confidential, as the number of products or notifiers are less than three for each pigment.

In a Danish consumer product project, Engelund and Sørensen (2005) looked into various shoe care products, including impregnation products, shoe polishers, tending products, cleaning products, liquid shoe polishers, fresheners, greases, oils and waxes. From examining the declared ingredients on 189 products, only two pigments were identified:

- C.I. Pigment Metal 1 (aluminium), CAS-no: 7429-90-5
- C.I solvent black 29 (RL), CAS-no: 61901-87-9

The report also provides an overview of pigments in "impregnation products" as extracted from the SPIN database of the Nordic Productregisters, as shown in the following table.

TABLE 28
PIGMENTS IN IMPREGNATION PRODCUTS AS EXTRACTED FROM SPIN BY ENGELUND AND SØRENSEN (2005)

CAS No	Chemical name	C.I name
51274-00-1	Iron hydroxide yellow	C.I. Pigment Yellow 42
147-14-8	Copper phthalocyanin	C.I. Pigment Blue 15
1314-13-2	Zincoxide	C.I. Pigment White 4
1328-53-6	Phthalocyanin Green	C.I. Pigment Green 42
6358-30-1	Diindolo(3,2-b:3',2'-m-)triphenodioxazin8,18-dichlor-5,15-diethyl-5,15-dihydro-	C.I. Pigment Violet 23
1317-36-8	Leaoxide	C.I. Pigment Yellow 42
13463-67-7	Titan dioxide	C.I. Pigment White 6
1333-86-4	Carbon black	C.I. Pigment black 6 og 7

It is also noted that red, yellow, orange and brown products might contain azo-dyes, including: C.I. Pigment Yellow 83, C.I. Pigment yellow 13, C.I. Pigment orange 13, C.I. Pigment red 224 and C.I. Pigment yellow 14.

No specific dyes or pigments were found in chemical analyses of a selected number of products, although content of Na, Al, S, Cl, Mn and Ba was interpreted as possibly originating from dyes or pigments.

Floor wax - Pigments used for car undercarriage products for professional use registered in the Productregister are shown in the table below. Titanium dioxide accounts for nearly 100% of the total.

TABLE 29
PIGMENTS WITH NON-CONFIDENTIAL CONSUMPTION IN CAR UNDERCARRIAGE AGENTS REGISTERED IN THE PRODUCTREGISTER

CAS No	Chemical name	Number of products	Number of notifiers	Registered consumption, average t/y *1	% of total
13463-67-7	Titanium dioxide	7	5	3.45	0.97
1314-13-2	Zinc oxide	15	8	0.11	0.03
	Other (2 confidential)	4	-		
Total incl. confidential				**3.57**	**100%**

*1 Registered consumption = content of registered products. Consumption = production/import - export. According to UCn Codes.

Metal polish - Data on pigments in metal polish in the Productregister are confidential as the number of products or notifiers is less than three for each pigment/application.

Car maintenance products - Carbon black is registered in five car maintenance products in the Productregister with a total consumption of less than 0.1 t/y. Data for two other pigments are confidential.

Undercarriage maintenance products - Pigments used for car undercarriage products for professionals registered in the Productregister are shown in the table below. The pigments in consumer products for the same application may be different as the products used by consumers, contrary to the products used by professionals, are typically provided in aerosols.

TABLE 30
PIGMENTS WITH NON-CONFIDENTIAL CONSUMPTION IN CAR UNDERCARRIAGE AGENTS REGISTERED IN THE PRODUCTREGISTER

CAS No	Chemical name	Number of products	Number of notifiers	Registered consumption, average t/y *1	% of total
1333-86-4	Carbon black	26	12	0.20	37%
1314-13-2	Zinc oxide	7	6	0.13	24%
1317-61-9	Triiron tetraoxide	4	3	0.02	3%
13463-67-7	Titanium dioxide	15	10	0.19	36%
	Other (2 confidential)	0	-	0.00	0%
Total incl. confidential				**0.53**	**100%**

*1 Registered consumption = content of registered products. Consumption = production/import - export. According to UCn Codes.

A6,6 Pigments and pigment preparations for colouration of construction materials and coloured mortar

Pigments used in products for colouration of construction materials and coloured mortar for professional use registered in the Productregister are shown in the table below. The table shows that about half of the amount of pigments for these applications is confidential as the number of products or notifiers is less than three for each pigment/application. Of the remaining amount, iron oxides account for the majority of the tonnage and titanium dioxide for a small amount.

TABLE 31
PIGMENTS WITH NON-CONFIDENTIAL CONSUMPTION FOR CEMENT, CONCRETE AND MORTAR REGISTERED IN THE PRODUCTREGISTER

CAS No	Chemical name	Number of products	Number of notifiers	Registered consumption, average t/y *1	% of total
1309-37-1	Diiron trioxide	54	8	155	23%
1317-61-9	Triiron tetraoxide	23	5	125	19%
13463-67-7	Titanium dioxide	40	18	21	3%
1317-80-2	Rutile (TiO2)			9	1%
147-14-8	C.I. Pigment Blue 15	5	4	0	0.0%
	Other (6 confidential)	23		354	51%
Total incl. confidential				**663**	**100%**

*1 Registered consumption = content of registered products. Consumption = production/import - export. According to UC62 Codes.

A6,7 Inks for pens and various types of pens such as ballpoint pens, felt tips, marker-pens, etc.

The only non-confidential pigment use in inks for pens (Danish: blæk) which can be extracted from the Danish Productregister is titanium dioxide in four products with a total volume of 0.2 t/y.

Data on other pigments in inks for pens (in total 12 pigments) and correction fluids (Danish: korrektionslak) in the Productregister are confidential as the number of products or notifiers are less than three for each pigment/application.

A6,8 Various – glow slime, snowflakes etc.

In a Danish EPA project on fluorescent substances in consumer products, Pedersen et al. (2003) looked at 24 different products.

Of possible relevance for the Danish Nanoproduct Register, zinc sulphide (CAS-no 1314-98-3) was declared as a pigment in Glow Slime and Finger Monsters.

Survey of products with nanosized pigments

The main focus of the study is on paints, wood preservatives, glues and fillers, as well as on coloured textiles. These are the types of products from which contained nanomaterials are most likely to be released under normal and foreseeable use.

In other words, the survey contributes to the overview of consumer products with nanomaterials on the Danish market. In addition, the project aims at discussing whether and which pigments may be considered nanomaterials according to the definition of "nanomaterial" recommended by the European Commission. This is done based on an initial mapping of pigments on the EU market.

Based on discussions with stakeholders, including trade organisations and industry, it is concluded that most pigments are likely candidates to be nanomaterials.

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