Optimization of PVC-free Materials in Cables

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Miljøstyrelsen vil, når lejligheden gives, offentliggøre rapporter og indlæg vedrørende forsknings- og udviklingsprojekter inden for miljøsektoren, finansieret af Miljøstyrelsens undersøgelsesbevilling.

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Draka-NKT Optical Cable A/S
5.7.2.3 Second Extrusion Trial................................. 40
5.7.2.4 Discussion of Results of the Second Extrusion Trial. 41
6. Environmental Evaluation of the Selected Materials
   6.1 The Summary of the Environmental Evaluation
7. Status for Halogen Free Materials for Cables
8. Conclusion
1. Introduction

This project has been carried out by DRAKA-NKT in co-operation with NKT Cables for The Danish Environmental Board in the period 1992-1995.

1.1 Scope

The scope of the project has been a further investigation into the possibilities of substituting PVC with Halogen Free Flame Retarded materials based on the results obtained in the previous project: Alternative to PVC in cables and connected building installations.

Special attention has been paid to minimizing those barriers towards increasing the use of the PVC-free materials, which were identified in the previous project i.e. primarily the processing difficulties encountered with these materials as well as their inferior long term properties in differing aggressive environments.

1.2 Follow-up Group

The project has been followed by a group with the following composition:

Jacob Brønnum, Miljøstyrelsen
Erling Bøje, Århus Kommunale Værker
Jørgen Bille Hansen, DSB Elektrotjenesten
Tom Nisted, Dansk Brandteknisk Institut
Svend Bank Andreasen, Telecom A/S
Flemming Hummelshøj Petersen, Københavns Belysningsvæsen

1.3 Project Progress

A large number of Halogen Free Flame Retarded compounds were selected for a thorough investigation of critical properties including long term properties in different environments.

At the same time the necessary computer software and knowledge have been established to simulate the relevant extrusion processes.

Based on the obtained results from the ageing tests three compounds were selected for further testing i.e. characterization of rheological properties, process simulation and later on test runs in the factory. The produced cables were then tested for mechanical properties and fire performance characteristics.

Preliminary tests were made on small optical cables produced on small extruders in order to minimize the material consumption. Experience obtained with these
small cables during the simulation and the production processes were then later on used in a larger scale production of power cables. Conclusions concerning the suitability of the established process conditions for the two cable types have been drawn. The possibilities of substituting PVC with Halogen Free Flame Retarded materials are considered.
2. Summary

During an earlier project concerning the possibilities of substituting PVC compounds in cables it was concluded that it is technically possible to substitute a significant amount of the current consumption of PVC for cables by Halogen Free Flame Retarded (HFFR) materials.

It was also concluded that there are important barriers towards the increased use of these types of compounds. These barriers are partly due to economical and partly technical reasons but the above mentioned project also stressed the fact that important material properties were not yet satisfactory to justify widespread use of the HFFR materials with the exception of indoor use without the influence of aggressive environmental factors. Furthermore the processing properties of these compounds were considered problematic.

The scope of this project has been to pave the way for increasing the substitution of PVC compounds by optimizing HFFR materials for cables. This was done by carrying out a material test programme aiming to identify the best possible candidates of HFFR compounds for cables and at the same time optimizing the extrusion process with the goal to increase the cable production line speed with these high viscosity materials.

The material test programme included 16 HFFR compounds and PVC compound which were all subjected to accelerated ageing in different environments at different temperatures in order to assess their use as candidates for the substitution of PVC compounds.

The outcome of the test programme was that compounds do exist which can substitute PVC compounds in several cable applications e.g. in buried cables at high humidity, cables in contact with oil at moderate temperatures, under the influence of sunlight etc. It also became evident that for applications in harsh environments special compounds which may have other limitations (e.g. flame retardancy properties) must be selected or developed, as is the case for PVC compounds.

It turned out that the HFFR compounds with the best overall properties were not among the easiest to process. This emphasizes the need for improving the processing equipment for HFFR materials i.e. design of screw and crosshead for extruder lines.

During the programme it was decided to use computer simulation as the method for optimizing the extrusion process. The result of the simulations was a new extruder screw design. Further the die geometry was adjusted which turned out to give significant process improvements compared to traditional machinery.
With the new production set up, optical test cables were produced with the compounds which had the best overall properties found during the material test programme.

The produced optical cable had good mechanical properties and also the flame retardancy behaviour was satisfactory.

Only the highly filled and due to that the HFFR compounds of the high viscosity type were able to fulfil the requirements for mechanical properties when used in power cable constructions.

The attempt to scale up the screw design which were used successfully during the production of optical cables on an extruder with an internal diameter of 63 mm to an extruder with an internal diameter of 150 mm and the length 18 times the diameter was definitely not successful.

Further a single flight screw for a 120 mm diameter extruder was tested within the programme without success.

With both screw designs the developed heat due to friction increased the mass temperature of the tested compound and caused thermal break-down of the HFFR compound within the extruders.

Screw designs for HFFR compounds have now become commercially available for extruders in the range of 100 - 150 mm diameter.
3. Background

The project is a continuation of an earlier project: Alternative to PVC in cables and connected building installations, carried out from 1990 to 1995.

The main conclusions drawn during this project were the following:

1. Halogen Free Flame Retarded cables will be more expensive than PVC based cables due to
   a) higher material price
   b) lower production speed due to much higher melt viscosity
   c) the compounds do not allow too high process temperatures

2. Outdoor use cannot yet be recommended
   a) for aerial cables because of too low resistance to UV light
   b) for cables buried in the ground in humid environments due to too high sensitivity to water.

3. Permanent contact with oils is not advisable.

4. Indoor use offers no technical problems.

5. The Halogen Free Flame Retarded materials (HFFR) are superior to PVC in case of a fire. Lower toxicity, corrosivity and smoke formation can be expected.

6. Cables with the requirement of flexibility cannot fulfil the requirement given in relevant specifications.

During the present project it is the intention to enlighten the above mentioned points further. The project has been divided in two simultaneously running parts:

1. A project for improving the processing of the materials

   and

2. A material test programme for selecting the materials with the best overall property profile.
4. Material Properties

Cable materials are normally characterized by an excellent long term stability which together with good mechanical properties secure a long cable service life regardless whether or not the end use will be indoor or outdoor under the influence of UV light, water or other environmental factors. PVC has a long and well established successful history as a cable material. It is necessary to specify and document corresponding requirements for other materials before they can be recommended for the use in cables.

The HFFR materials are far from being as well evaluated. Standards already exist with requirements for the short term properties supplemented with very mild ageing tests which in no way qualify materials for practical outdoor use. Thus we have found it necessary to set up a test programme which really gives information about the long term properties.

Part of the test programme originates from the results obtained during the previous project, but it has been changed at some critical points e.g. an oil ageing test at 50°C has been added. In this way we get a better impression of the possibilities of using the materials in contact with oil and vaseline.

We have chosen to perform dry ageing at high temperature to make sure that the basic resistance to thermal ageing/oxidation is acceptable.

Ageing test in water at pH 4 and pH 7 have been carried out in order to simulate the environment for cables buried in the ground. The experience from the previous project in fact was that degradation in wet ground conditions seemed to happen faster than in the laboratory water so new tests simulating the burial of cables under different soil conditions, or even better actual test on cables buried in the ground are needed. It has not been possible during this project to put cable samples in the ground. However, we needed to carry out the ageing test in water.

This time we have neglected the salt water test which turned out to be less severe than the test in tap water at pH 7.

The ozone test is traditionally carried out for rubber compounds and polymers with unsaturated groups which are sensitive to ozone but this test is specified for HFFR sheathed cables also.

Stress crack resistance is also a traditional test carried out due to stress cracking problems in polyethylenes many years ago. When new and comparatively unknown materials are introduced this test is still considered essential.

Testing under the influence of UV light is necessary in order to make sure that cable sheathings can resist the climatic condition when the cables are stored or used outdoor and do not degrade too fast.
For the evaluation of the influence of ageing on the materials the change in mechanical properties are used as parameters for characterisation. Important information can also be obtained from measuring the weight change of test samples after ageing in the different media.

### 4.1 Test Plan

The 15 originally selected compounds have been tested according to the following scheme:

**Long Term Properties**

- Dry ageing in heat ovens at 100 and 120°C.
- Ageing in water at pH 4 at 20, 50, 65, 80 and 95°C.
- Ageing in water at pH 7 at 20, 50, 65, 80 and 95°C.
- Ageing in ASTM no. 2 oil at 20, 50, 80 and 100°C.
- Ageing in cable vaseline at 20, 50 and 80°C for selected compounds.
- Ozon test according to Cenelec HD 22.2 S2. Test period prolonged compared to the standard.
- Environmental stress corrosion test according to ASTM 1693 in Antarox CO-630 solution, 10%.
- Ageing in QUV Test chamber using the following cycle: 20 hours UV light followed by a 4 hour water condensation period.

**Burning Properties**

- Measurement of Limiting Oxygen Index (LOI) according to ASTM 2863 and modified LOI, the latter giving better correspondence with actual fire tests.

- Smoke corrosivity test according to IEC 754-2.

- Flame propagation test according to IEC 332-1 and IEC 332-3-C (“small” and “big” IEC fire test). These tests are performed only on cable samples produced in part 2 i.e. with the especially selected compounds.

- Smoke density according to IEC 1034.
4.2 Selection of Materials

During the previously mentioned project four materials, designated 54003, 80465, 80476 and 80260 were evaluated. The one with the highest flame retardancy, 54003, turned out to have an extremely low resistance towards ageing in water, the flame retardance properties of 80465 were too low for use in an optical cable construction with flammable core to pass the IEC 332-3-C fire test, 80476 which had very good long term ageing properties was too difficult to extrude on existing machinery and 80260 was not stable enough towards UV radiation.

These results suggested that a larger number of compounds had to be examined in order to secure that the compounds which were best suited for the application were included in the programme. It was of course also of interest to evaluate the results of the ongoing development work carried out by the material suppliers.

After a survey of the available raw materials, 16 compounds were selected. In the following they will be referred to by the numbers from 1 to 16.

No. 1-3. The first three materials are not commercially available compounds. They are test compounds produced by NKT Cables i.e. with known composition and included in the test programme due to that reason, so conclusions taking the composition into account can be drawn from the results obtained with these materials.

The remaining compounds are all commercially available and only very limited information of the actual formulations are available to us for these compounds.

No. 4. Selected because it fulfills VDE 0207 HM 4 specification and has a reasonable price.

No. 5. Based on polypropylene and is therefore expected to have a very good performance in wet environments.

No. 6. This was selected because of promising data sheet values, price and the possibility to crosslink the compounds chemically. Crosslinked material should have better resistance towards aggressive media.

No. 7. Interesting product with claimed good processing properties combined with high content of flame retardant filler and good UV stability.

No. 8. Black compound, should therefore be well suited for outdoor use (UV stability).

No. 9. An easy processing compound with a low degree of flame retardancy and very low price.
No. 10. This compound was selected due to stated good resistance towards water and high temperatures.

No. 11. A widely used compound with a good combination of properties.

No. 12. This material was the only non black compound with a high UV stabilisation. Further, it had good merits with regard to acid resistance which gives good possibility for use in wet areas also.

No. 13. Claimed properties close to those of compound no. 14, but with lower filler content and better processing properties.

No. 14. This material is identical to material 80476 from project 1, which showed very good long term properties and low price level. It is included again and dealt with especially in the processing part.

No. 15. Included due to the very good resistance towards water.

No. 16. A substitute for 54003 in project 1. Highly flame retarded but expensive. It is included as it may be the only candidate in a cable construction that can pass the IEC 332-3-C test as a cable jacket around a flammable core.

No. 17. Two crosslinkable materials have also been selected for testing in oil. One of those is material no. 6 but crosslinked, and the other is a material especially developed for use at high temperature but good chemical resistance is also expected.

18. As a reference a standard cable PVC compound has partly been included in the test programme.

Fig.1 Light Duty Optical Cable

4.3 Test Results

4.3.1 Experimental

The compound test samples were extruded on a Brabender Extrusiograph (lab. measuring extruder). Approximately 1mm thick bands were extruded through a
slit die at the temperature recommended for the compound by the suppliers. Afterwards standard tensile dump-bells were punched from the bands.

All of the compounds, except material no. 5, were successfully extruded with a smooth surface and homogeneous appearance. No. 5, however, turned out to cause two problems. Firstly a very unpleasant smell from the hot compound and secondly the band looked rough with brown dots in the surface. The samples were then aged in the different media and tested at predetermined intervals. As a standard the tensile strength (TS) and the elongation at break (EB) were measured and also the weight change of the samples after different immersion times in the individual media was measured.

The ozone and stress cracking tests were completed as previously described (section 4.1). Based on the results obtained from the ageing tests each material was given a mark between 1 and 6 for each test environment in order to simplify the ranking of the compounds which will be carried out, see table 4.

4.3.2 Dry Ageing Tests

The results of the dry ageing tests are shown in appendix 1.1 to 1.6 for the whole range of HFFR compounds. As a failure criteria the elongation at break value below 100 % or tensile strength value below 10 MPa were used. The resistance to dry ageing of all the compounds was excellent. Only in one case, material no. 1 at 120°C after 40 weeks ageing, was a low value found, i.e. elongation at break was 92%, just below the limit. Because of the lack of observed failures it is not possible to extrapolate the life times at low temperature from the accelerated heat oven tests. We can just note that the retained mechanical properties after 40 weeks’ ageing at more than 100°C are very good.

In typical specifications 10 days at 100 or 110°C is considered satisfactory. Dry ageing tests of two standard PVC cable compounds show that the 100% EB is typically reached after approximately 100-200 days at 110°C, see appendix 1.6. Two materials, nos. 9 and 13, were only tested at 100°C because their melting point was lower than 120°C.

The results confirm the conclusion of project 1, i.e. the thermal stability of all the compounds is good enough to secure the cable reliability for applications with no contact to harsh chemicals i.e. normal indoor use. For indoor use the expected lifetime of HFFR materials even seems longer than that of standard PVC compounds, depending on the thermal load.
Fig. 2. Typical ageing plot

### 4.3.3 Wet Ageing Tests

High priority has been given to the tests in water because it is considered necessary to find materials with a good chance of a long service life in wet soil. Ageing has been carried out in water at pH 7 and pH 4 at 20, 50, 65, 80, and 95°C. Ageing times from 0 to 40 weeks. The degradation was evaluated by measuring the tensile strength as well as the weight change.

#### 4.3.3.1 Water pH 7

All the results from the water ageing at pH 7 are shown in appendices 2.1 to 2.17. Contradictory to the dry ageing this test series shows remarkable differences in resistance to water, pH 7.

Already at 20°C failures are observed. After 8 weeks material no. 7 has virtually no elongation at break left and after 28 weeks the same is the case for material no. 10, which among other things was selected due to its claimed good water performance. Material no. 16 failed after approximately 15 weeks. These compounds cannot be used under wet conditions.

At 50°C the compounds nos. 1 and 8 show unacceptable resistance towards the water. Material no. 8 would have been a nice choice for general outside use but the water resistance is inadequate. A common feature for the four mentioned materials is that the filler is Mg(OH)$_2$, which also during project 1 seemed to be connected to inadequate water performance.
At 65°C also material no. 4 fails with low EB after 4-8 weeks.

Material no. 15 has reached its limit at 80°C and at this temperature nos. 6 and 11 are also marginal.

Compounds nos. 3 and 12 cannot resist water at 95°C but the remaining materials nos. 2, 5, 9, 13, 14 and standard PVC still have acceptable mechanical properties after 40 weeks ageing at 95°C in water at pH 7.

The water absorption measurements are also shown in appendix 2. Attempts to correlate the amount of absorbed water with the decrease in mechanical properties were not successful. We have cases where the elongation at break is low for a sample with a small amount of absorbed water and also the opposite i.e. a significant weight increase resulting in no mechanical degradation has been seen.

As an example of the water ageing fig 3 and 4 show the degradation of materials nos. 7 and 14 in water at pH 7 at 20 and 95°C, respectively. Fast degradation is observed at 20°C for no. 7 while no. 14 is still shows very good value after 40 weeks at 95°C. Note that this is revealed by the elongation at break (fig 4) but not the tensile strength results (fig 3).
4.3.3.2 Water pH 4

An identical test programme has been carried out in water with a buffered pH value of 4. The results are shown in appendices 3.1 to 3.15.

The compounds can be divided into two groups with regard to “behaviour” in water at pH 4.

For the first group no difference is seen between the two pH values. This group includes the following compounds nos. 2, 3, 4, 5, 6, 7, 9, 13 and 14. In the other group three materials behave very differently in the two media, nos. 1, 8 and 10 are very stable in pH 4 and very unstable in pH 7 water. The remaining nos. 11, 12 and 15 are a little more stable in pH 4 than in water at pH 7.

The reason that for some materials water at pH 4 is a more “healthy environment” than water at pH 7 can be linked to the actual pH, but since the acidity seems to be an advantage we find it more likely that the ionic strength or osmoticity is an important factor. A concentration of solutes e.g. as found in the pH 4 solution simply lowers the activity of the water molecules and thus the resistance of the compound is improved. Again the effect seems to be present for the compounds that contain Mg(OH)$_2$ in particular.

Fig 5 shows the behaviour of compound no. 8 in the two different media at 50 and 80°C, respectively.
Concluding the water tests it can be stated that just like for PVC compounds it is possible to find HFFR compounds that can survive 40 weeks in water at 95°C and different pH values. These materials can be used as sheathing compounds for cables in wet areas with a good possibility of a long service life.

4.3.4 Oil Ageing Tests

The oil ageing tests were performed in a similar manner to the water ageing tests with ASTM oil no. 2 replacing the water. The maximum test time was again 40 weeks, and the strength as well as the oil absorption/extraction values were measured. The results are shown in appendices 4.1 to 4.19.

At 20°C, all the compounds show very good mechanical properties. Materials nos. 1, 5, 7, 8, 13, 14 and 15 have survived 40 weeks with property changes below 20%. The remaining materials have changes between 20 and 40% except no. 11 which has an EB below half of the original value but still well above 100%. All the materials had oil absorptions around 5-10% by weight after 40 weeks, except no. 15 which absorbed only 2% by weight. Strangely enough material no. 15 had been chosen due to its acclaimed water resistance but in oil it showed an exceptionally low absorption. Already this low temperature test suggests that all the materials are acceptable for non-permanent oil contact applications and some even for long time in contact with a moderately aggressive test oil.

At 50°C, the oil absorption level is increased but now it varies very much from one compound to the other, the lowest being 10% (material no. 15) and the highest absorption 54%. The tensile properties retained are still acceptable for most compounds, the standard PVC compound included. After 40 weeks all EB values are above 100%. Some have become rather week, however, especially
nos. 11 and 16 with approx. 25% of their original tensile strength left. Material no. 15 still shows exceptional values after ageing at 50°C.

The 80°C test lasted only one week because of failure of the equipment. However, the duration was long enough to show that some materials simply dissolve in ASTM no. 2 oil when they get close to their crystalline melting point. Some compounds retain marginal strength. These are nos. 5 (because it is polypropylene based), 10, 14 and 15, which nearly behave like a cross linked material retaining a very high tensile strength.

The test at 100°C gave similar results showing that nos. 5, 10 and 15 are still behaving like polymer materials even after 28 weeks exposure.

If we compare with standard cable PVC compounds we typically see that after one week at 95°C their EB drops near to 0 while the strength is doubled. Both these observations are due to loss of plasticizer but show that the best HFFR materials clearly match the standard PVC with respect to oil resistance. Special oil resistant PVC compounds exist which give much better results as the plasticizer is non-migrating. These types are more expensive and often stiffer than standard PVC compound and consequently only used when really required.

Concluding the results of the oil tests we may say that both standard HFFR and PVC materials have a reasonable resistance towards immersion in ASTM test oil no. 2. In both types of compounds especially developed compounds exist that will perform for a longer time with permanent oil contact.

### 4.3.4.1 Effect of Cross Linking on Oil Resistance

Some of the HFFR compounds have a polymer composition which makes chemical cross linking possible. By cross linking it is possible to form a 3-dimensional molecular network which is normally assumed to give better mechanical and thermal properties as well as chemical resistance than in corresponding thermoplastic material. The disadvantage from an environmental point of view is that recycling of cross linked materials is not possible. As the cross linking process of the compounds chosen in this project is of the so-called silane cross linking type, the processing itself is also more problematic because it involves the addition of a catalyst masterbatch (granules or liquid) before extrusion, and a treatment in hot water or steam afterwards in order to obtain a proper cure stage.

Material no. 6 was cross linked by this method as well as a 17th compound especially designed for silane cross linking. A hot set test made at 200°C showed that for both compounds the cross linking reaction was successfully carried out.

The results from the ageing tests are shown in appendix 4.19. The results obtained for no. 6 show that cross linking has an effect on the oil resistance. Fig. 6 shows the degradation of cured and uncured samples of
material no. 6 in ASTM Oil no. 2 at 65°C. The uncured sample loses nearly all its tensile strength while the cured sample retains about 30% of the original strength.

Sample no. 17 (appendix 4.19) shows an oil resistance as good as the best thermoplastic materials above but not more than what had been accomplished by carrying out the cross linking process.

The theoretical advantages of cross linked materials have been verified by the experiment with compound no. 6, but no real advantage has been achieved in comparison with the best compounds from the group tested. Consequently, it was chosen not to continue the evaluation of cross linked materials in this project.

4.3.5 Ageing in Cable Vaseline

In order to make communication cables water tight they are often filled with cable vaseline (petro jellies). These consist of natural hydrocarbon oils thickened with microcrystalline wax and in project 1 “Alternative to PVC in cables and connected building installations” the materials tested were non compatible with vaseline except for material 80476 (no. 14 in this project). The test temperatures were 20 and 80°C then, this time we also have carried out measurements at 50°C.

Only four materials were tested in vaseline. These being the most interesting compounds based upon an overall evaluation of the properties, i.e. materials nos. 6, 9, 11 and 14. The results (see appendix 5.1 to 5.4.) do not differ very much from those which were observed in the oil ageing tests. Good stability at 20 and
50°C and degradation after short time at 80°C except for no. 14 which after 40 weeks at 80°C has retained above 10 MPa in TS and 86% in EB.

Thus it seems that it is safe to use no. 14 in jelly filled cables and probably also nos. 6 and 11 based upon the good results obtained at 50°C. No. 9 should probably be avoided for this use because of a rather high absorption (11% at 20 and 28 at 50°C).

Fig. 7 shows the decrease in tensile strength for compound no. 11 as a function of time and temperature.

**Fig 7. Material 11 in Cable Vaseline**

<table>
<thead>
<tr>
<th>Time [weeks]</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
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<tbody>
<tr>
<td>Tensile strength [MPa]</td>
<td>14</td>
<td>12</td>
<td>10</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

### 4.3.6 Ozone Resistance

Ozone is present in atmospheric air in small amounts and in certain environments in larger amounts. Ozone is a very reactive gas, especially towards double bonds in some polymers causing chain breakdown.

Standards exist which specify the requirement of a certain ozone resistance for vulcanized cable compounds and also for the HFFR materials even if the polymer used are without double bonds. Stressed samples of the compounds are placed in an atmosphere with 200 ppm ozone for 14 days (normal requirement is 40 hours) and later on inspected for any sign of cracks. One of the samples, material no. 7, had small surface cracks but none of the others showed any sign of complete damage.
4.3.7 Stress Cracking Test

The tendency of the materials to environmental stress cracking has been tested according to the "Bell Test", ASTM 1693. Stressed samples are placed in contact with a 10% Antarox CO-630 solution at 50°C and examined for the formation of cracks.

None of the samples showed any sign of stress cracking.

4.3.8 UV Ageing Test

Accelerated UV ageing and weathering was performed with the selected materials. The QUV Tester used was equipped with UV 340 lamps with a spectral distribution very close to that of sunlight. The test cycle used was 20 hours UV light at a black panel temperature of 60°C followed by a 4 hour water condensation period at a black panel temperature of 50°C. Based on experience with different plastic materials an acceleration factor of about 50 is assumed (compared to Northern European Climate).

Preliminary test

The test samples were extruded bands of materials nos. 1-15 without addition of colour masterbatch. The ageing was again measured by the decrease in tensile strength. The first samples were examined after 4 weeks exposure and the last ones after 43 weeks. The results are given in appendix 6.

Large differences between the individual compounds were observed. Nos. 6, 10 and 14 were below 100% in EB already after 4 weeks, followed by nos. 1, 7 and 11 (5-10 weeks). The next group of compounds were nos. 2, 3, 4 and 15 which failed to fulfil the criteria between 10 and 28 weeks while nos. 5, 9 and 13 lasted more than 28 weeks before the 100% EB/10MPa TS criteria was passed. The two remaining materials nos. 8 and 12 were both OK after 43 weeks ageing corresponding to something like 40 years of outside service if the assumed acceleration factor is correct.

These two materials are good candidates for permanent outdoor use. They are also the only two which were UV stabilized by the supplier, no. 8 being black and no. 12 containing a stabilization package which made colouration of the compound difficult due the compound’s initial colour.

Evaluation of addition of stabilizers

In order to investigate the effect of UV stabilizing additives we have selected material no. 14 for further examination. This material exhibits the best overall property profile except the stability against UV irradiation which is very bad thus offering a good opportunity for testing the additives.

Material no. 14 was tested during UV irradiation in 5 formulations
1. Without additives.
2. With an addition of 2% blue colour masterbatch.
3. With 2% blue and 1% HALS (Hindered Amine Light Stabilizer).
4. Same as 3 + 0.5% UV absorber.
5. With 2% blue and 1% of another HALS type.

The results are given in fig. 8.

The results are very clear. The unstabilized version of the compound is, as in the preliminary test, degraded after 5 weeks (EB 21%) while all the others are OK even after 38 weeks corresponding to nearly 40 years. So it seems that just the addition of colour pigment is enough to obtain good stability against UV irradiation.

Experiences from other areas indicate that such long term extrapolations are always dangerous and therefore it is advisable always to add a UV stabilizing additive for permanent outdoor applications. It is also doubtful whether or not all pigments offer the same protective effect as the blue pigment tested. We assume that the observations made for material no. 14 are general, but of course it will be necessary to carry out a test against UV irradiation with the actual compound to be used.

Tests on standard PVC compounds in a grey colouration show that EB 100% is passed after 7-12 weeks. But it is known that a cable sheath based on such a PVC compound will typically last 20 years before getting brittle. Based on the QUV tests we would expect UV-stabilized HFFR types to be at least as good as standard PVC which has been in use for outdoor use for many years.
4.3.9 Burning Properties

The Limiting Oxygen Index (LOI) has been determined for all the compounds as well as the “modified” LOI value using a proprietary method which gives better correspondence with actual fire tests behaviour than the traditional LOI measurement. The higher the LOI value, the smaller is the tendency to support a flame in a fire situation.

Also the corrosivity of the smoke has been tested according to IEC 754-2, which requires a pH value higher than 4.3 and a conductivity lower than 100µS/cm in the wash water from the smoke test.

Results from the fire tests in table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LOI % ASTM2863</th>
<th>LOI mod. %</th>
<th>pH IEC 754-2</th>
<th>Conductivity, µS/cm IEC 754-2</th>
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<td>16</td>
<td>49</td>
<td>34</td>
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<tr>
<td>PVC</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

* Data from supplier’s data sheet.

From the results above it is obvious that the fire retardancy judged by the LOI value varies a lot from one compound to the other. Using the modified LOI for ignitability, however, we see minor differences, but still we can see different levels of ignitability. Material no. 16 is clearly the best (i.e. the most difficult to ignite). Then we have an intermediate group and at last a group with very low fire retardancy consisting of nos. 10, 12, 13 and 15.
The corrosivity tests show that all the HFFR materials tested, except no. 5, easily pass the two requirements. Material no. 5 is probably retarded with ammonia polyphosphates explaining why the smoke conductivity is so high.

4.3.10 Processing Properties

Initial measurements of the melt viscosity have been carried out on a measuring extruder, see chapter 5.3. Based upon these measurements the individual compounds can be classified with regard to processability.

4.4 Discussion of Results

In table 2 we have tried to give an overall view of the test results mentioned previously. For the long term tests we have found it convenient to characterize the ability to withstand the influence of given environment conditions by a number between 1 and 6. 1 representing a totally unsuited material for the actual end use and 6 the best choice for permanent use under those environmental conditions. In this way we have an easy method for selecting the best material for a given end use. For the more detailed evaluation and the possible life time predictions, it is necessary as the next step to consider the degradation graphs given in the appendices.

Below the methods for characterizing the properties by marks are described.

**Ageing in heat oven**
6 is given if no changes in properties are observed after 40 weeks at 120 and 100°C, respectively.
If the tensile strength (TS) is still above 10 MPa and the elongation at break (EB) still better than 100% a mark of 5 is given.
Because of the good results it was unnecessary to use marks below 5.

**Ageing in water**
6: TS above 10 MPa and EB above 100% after 40 weeks at 95°C.
5: Same requirement after 40 weeks at 80°C.
4: Same requirement after 40 weeks at 65°C.
3: Same requirement after 40 weeks at 50°C
2: Same requirement after 40 weeks at 20°C
1: Failure before 40 weeks at 20°C.

**Ageing in ASTM oil no. 2**
An evaluation is given for each of the temperatures tested.
6: No change in TS and EB after 40 weeks
5: Changes below 20% compared to original values.
4: Changes between 20 and 40%.
3: Changes above 40%.
2: Material strongly degraded but still coherent and measurable.
1: Material disintegrated and not measurable in a tensile test.
Ageing in the QUV apparatus.
6: No changes in TS, EB and surface gloss after 40 weeks in QUV Tester.
5: Changes below 20% and surface gloss intact after 28 weeks.
4: EB above 100% after 28 weeks but surface degraded.
3: EB below 100% within 10-28 weeks.
2: EB below 100% within 5-10 weeks
1: EB below 100% before 5 weeks.

Concerning processability the compounds are classified according to viscosity level measured at 100 s\(^{-1}\) at processing temperature.

6: Viscosity below 500 Pas
5: Viscosity from 500 to 1000 Pas
4: Viscosity from 1000 to 1500 Pas
3: Viscosity from 1500 to 2000 Pas
2: Viscosity from 2000 to 2500 Pas
1: Viscosity above 2500 Pas.

The results from the fire and smoke tests in table 1 are simply given as “pass” or “fail” according to the relevant standard test procedure.

As stated in table 2 and in the preceeding paragraphs there are great variations between the individual compounds. Some have extremely good properties in one respect and very poor properties in another. We have a compound with excellent stability to oil at high temperature, one with excellent UV stability and several with excellent resistance to water. None of the compounds are optimal in every respect but neither is PVC. It is in fact possible to find a compound with as good overall properties as PVC and, naturally, improved fire performance.
<table>
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<td>1</td>
<td>3</td>
<td>6</td>
<td>2-3</td>
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</table>

* The UV results (except for nos. 8 and 12) are for uncoloured and unstabilized compounds. See results for stabilized versions in section 4.3.8.
4.5 Selection of Compounds for Further Studies

Based upon the results from the material test programme 3 compounds with overall acceptable general properties have been selected for further study of the processing properties and for the production of different test cables and finally fire testing.

The selection process follows a stepwise exclusion method as follows:

1. The first requirement is that the compound must be commercially available. Hereby we can exclude materials nos. 1, 2 and 3 which are all development products.

2. The next general requirement is that the fire retarding properties must be sufficiently high. Our best criteria before making real fire tests is the determination of modified LOI value. Values below 26% we characterize as low. 27-32 medium, and values >33 as highly fire retardant materials. Setting the limit to 26% minimum we can exclude the compounds nos. 10, 12, 13 and 15. Still remaining are nos. 4, 5, 6, 7, 8, 9, 11 and 14.

3. Another basic requirement is that the combustion smoke must fulfil the corrosivity specifications in IEC 754-2. Compound no. 5 which maybe has the best overall properties, clearly exceeds these requirements and must be excluded. In fact it turned out later on in the project that this compound is still to be considered as a developmental product due to the inhomogeneities described in 4.3.1.

4. Of the remaining 7 materials nos. 4, 7 and 8 showed rather bad resistance to water at different temperatures. This made the application for buried cables very doubtful and thus these compounds are excluded.

5. The level of fire retardancy of compound no. 9 is significantly lower than for nos. 6, 11 and 14. For this reason we chose nos. 6, 11 and 14 in spite of the good overall properties of compound no. 9.

6. We have 3 compounds left. As stated in table 2 the UV stability of these compounds are unacceptable. For this reason UV tests with coloured and stabilized versions of compound no. 14 have been carried out and the results look that good that permanent outdoor use seems realistic (fig. 8). We believe that this result will also be valid for the other HFFR compounds. Compound no. 14 is superior to the other two regarding contact to water, vaseline and oil. Expecting extrusion difficulties with no. 14 we have found it necessary to include also nos. 6 and 11 for further studies. These two, especially no. 11, should be more easily processable.

The price level for the three materials is at the lower end which is also an important parameter.

In the following parts of the report the processability of the HFFR compounds are treated with special focus on the three selected compounds.
5. Processability

5.1 Background

The HFFR compounds are more difficult to process than conventional polymer materials like plasticized PVC, PE etc. This is due to two main reasons. Firstly, the HFFR compounds contain high loadings (up to approx. 65%) of inorganic fillers in order to achieve good flame retarding properties. This means that only a limited part of the compound is polymeric and for this reason the melt viscosity gets very high. Consequently, large shear forces are developed and high frictional energy is created in the extruder during processing giving rise to undesired temperature rises in the compound. The higher the extrusion speed, the higher the heat build up during the extrusion process.

If the temperature gets too high the fillers (hydroxides) liberate water (crystal water). This has three main effects:

1. Development of bubbles in the product and the surface gets rough.
2. The flame retarding effect of the fillers is reduced.
3. The mechanical properties cannot fulfill the requirements.

Thus it is important to keep the temperature as low as possible during processing. For this reason the polymer part of the compounds has been selected with as low crystalline melting points as possible with due respect to other essential features like mechanical and thermal deformation properties, compatibility with filler, chemical stability etc.

Other problems are obtaining a good mixing with colour masterbatch and often also the build-up of large deposits at the die opening.

The main challenge is to find ways to increase the line speed of the extrusion processes to “PVC” like level, maintaining good quality of the extrudate and without overheating the compound.

5.2 Strategy

The challenge can be dealt with in different ways. One is to select the materials with the best processing properties i.e. the lowest melt viscosity. The lowest viscosity is, however, frequently related to the lowest flame retardancy due to low filler concentration.

Another way is to try to optimize the machinery (extruder screw, distributor and die) in such a way that temperature is kept low also at high line speeds.

Normally, the best way forward will be a combination of the two, selecting as “friendly” a compound as possible, still with adequate flame resistance (and other properties, see section 4) and also optimize the processing equipment which normally consists of standard parts. These parts have typically been optimized for general purpose materials like PVC and PE which very seldom present processing problems of the type mentioned.

Due to the many variables involved in the extrusion process it is extremely difficult to foresee the effect of a given adjustment i.e. will the effect of increased temperature settings on the extruder be a higher or a lower
melt temperature? The obvious answer is “higher” but in fact it depends on a lot of things like the relative amounts of frictional and conductive heating, the temperature dependence of melt viscosity etc.

Due to the high complexity of the problem we have chosen a new solution method i.e. computer simulation of the extruder process making it possible to perform test runs on a computer for a short time instead of the time and money consuming trial and error testing in the factory.

After having selected the final compounds based on the material test programme the idea is to perform computer simulations with these materials in order to design an optimal extruder screw, distributor and die system for a 63 mm conventional extruder.

Comparative test runs are then to be made with new and conventional equipment.

5.3 Initial Rheological Characterization

Before any attempts to perform computer simulations it is necessary to determine the rheological properties of the individual compounds.

The initial rheological characterization of the compounds was made on a Brabender Extrusiograph measuring extruder. For every compound the recommended processing temperature was chosen for the measurement. The molten compound was extruded through a die of well defined geometry, readings of output and corresponding pressure drop were made and converted to shear viscosity vs. shear rate flow curves.

From the curves the viscosity values have been taken at a shear rate of 100s$^{-1}$. The results are shown in table 3.

The measurements only give a rough comparative classification of the processability since the measurements were made at one temperature only and at a rather low and limited shear rate range.

Closer rheological studies were made with the three selected compounds nos. 6, 11 and 14. The simulations for these are described in chapter 5.6.
### Table 3.

<table>
<thead>
<tr>
<th>Compound no.</th>
<th>Viscosity (Pas) at 100 s⁻¹</th>
<th>Measured at (°C)</th>
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<td>-</td>
</tr>
<tr>
<td>2</td>
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<td>15</td>
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</table>

### 5.4 Introduction to Computer Simulation

Three commercially available software packages for the simulation of the extrusion process have been evaluated and tested at the supplier’s work stations. The one giving the best data agreement with the values measured on the Brabender Extrusiograph was chosen. It was the package from Polydynamics Inc., Canada and Compuplast, Czech Republic consisting of the Polycad programme for general 2-dimensional flow analysis, the Extrucad programme for simulating the extrusion process, and two accessory programmes for viscosity data processing and storage, Viscofit and Polybank.

A computer simulation using these programmes proceeds as follows:

1. Measurement of viscosity data i.e. Rabinowitch corrected shear viscosity and elongational viscosity as a function of shear rate and temperature.
2. Fitting the data to viscosity model (Newtonian, Power Law, Carreau etc.) using Viscofit.
3. Polycad simulation of flow in the die and the distributor, primarily to find the pressure necessary for a given extruder output. This simulation is based on the iterative solution of balance equations for heat, mass and momentum and apart from the flow properties it is necessary to know melt density, heat capacity and thermal conductivity. Further the geometry of the die and the distributor, temperature settings and melt temperature must be given.
4. Extrucad simulation of the extrusion process using the above mentioned exit pressure, screw RPM, temperature settings and extruder geometry as input parameters. Also the properties of the solid compound must be given i.e. the crystalline melting point, the heat capacity, the bulk and the mass density, the heat of melting and also friction coefficients of granules against the metal surfaces of the extruder. The result of the simulation includes all relevant pressures, temperatures, stresses, rates, degree of melting, and heat and mass flows as a function of position in the extruder.
5. Normally the extruder output at the selected screw RPM and the assumed output through the die will not be in agreement. This must be accounted for by adjusting the RPM until the agreement of flow is achieved. Also adjustment of the input melt temperature in the die must agree with the exit temperature of the extruder. After a few adjustments of the data and new simulations the agreement will normally be reached.
6. The data are then evaluated and for the actual compounds the most important item was to make sure that the compound was not overheated and that the extruder motor was not overloaded.

5.5 Mixing Tests

5.5.1 Background

The normal method for colouration and UV stabilization of polymer compounds is mixing with concentrates, masterbatches. In order to get a good distribution of pigment or stabilizer the viscosity of the masterbatches is normally very low. For the very viscous compounds involved in this project this gave problems as a very highly viscous melt does not mix well with a nearly liquid one (viscosity mismatch). Also in the cross linking of HFFR compounds where an optimum mixing is essential this point is relevant. One way of solving this without having to use especially developed concentrates is to use mixing elements in the extruder screw for improving the distributive mixing of colour in the HFFR compound. In the following section a trial series of such elements is described.

5.5.2 Mixing Experiment

On the Brabender Extrusiograph a 19 mm screw was designed in such a way that the last 3L/D of the 25L/D screw could be exchanged. Three elements were tested, first the normal metering zone without mixing elements and then two types of mixing element.

Two of the compounds were tested, one with a rather low viscosity, 80465 and one with a higher viscosity, compound no. 6.

The results were very clear. The normal screw gave a poor mixing with distinct concentric rings of colour in the extruded round rod whereas the mixing units of both types gave better results with rings that were scarcely noticeable under microscope at 100x magnification of a thin section in transmitted light, see appendix 7. No significant difference between the two tested compounds was seen.

5.6 Computer Simulation in Practice

5.6.1 Rheology - Testing and Modelling

For the computer simulations the rheological characterization was made on a Rosand Precision Capillary Rheometer on the compounds nos. 6, 11 and 14. Measurements were made at two temperatures (160-180°C) and a range of shear rates between 20 and 20000s⁻¹.

For the shear viscosity the Carreau model was chosen in order to take the lower Newtonian flow region (which is neglected by the Power Law) into account in the simulations. The elongational viscosity was modelled by the Power Law. For all three materials the flow properties are given by the following equations:

Shear viscosity as a function of temperature and shear rate \( \dot{\gamma} \):

\[
\eta(T, \dot{\gamma}) = \frac{K \times e^{-b(T-T_i)}}{(1 + (C \times e^{-b(T-T_i)} \times \dot{\gamma})^a)^{(1-n)/a}} \tag{1}
\]
Elongational viscosity as a function of elongational rate $\dot{e}$:

$$\eta_e(\dot{e}) = E \times (\dot{e})^{n_e-1}. \quad (2)$$

$K$, $b$, $C$, $a$, $n$, $E$ and $n_e$ are constants determined by the Viscofit programme for each of the compounds. $T_r$ is an arbitrary reference temperature.
Table 4

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<tr>
<td>Heat cap.(solid)</td>
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<td>Heat of melting</td>
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<td>15000 J/kg</td>
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The determined values of the constants are given in table 4 together with the other necessary properties.

5.6.2 Process Simulation

The extrusion tests were carried out on a 63 mm extruder with an L/D ratio of 22. It was originally equipped with standard PE and PVC screws and a head with distributor and die optimized for standard materials like PE and PVC. From the very start it was evident that optimization of the processing of the selected HFFR materials meant changes in the extruder geometry.

First the die was considered. Simulations showed that with a conventional die a given output of material no. 14 could be obtained if the pressure at the die entrance was approx. 70 MPa. After a few attempts of adjusting the die geometry a die with the same hole geometry was constructed that could transport the same amount of compound at a pressure of 24 MPa. At the same time the maximum temperatures were decreased due to the changes which were primarily opening of flow channel giving lower shear heating. The same procedure was followed for the distributor resulting in a pressure drop of 4 MPa for this part and a total of 28 MPa at the exit of the extruder.

This final pressure was used in the simulations of the extrusion process. Simulations were made with a lot of screw designs and finally (after approximately 100 simulations) the design of a new screw was decided. This screw gave an acceptably low melt temperature, total melting already at 14D from the entrance to the extruder and a torque manageable for the extruder at the desired output rate which was 2-3 times higher than what could be obtained with the normal screws.

5.6.3 Test Runs on Extruder

These simulations formed the basis for the construction of a new screw, called the “Extrucad” screw in the following. Among other features defined through the simulation the new screw contains a mixing zone with a length of 3D at the end of the screw.

Comparative test runs were then carried out with five materials and the three available screws in order to see the results of the simulation procedure in practice. The results are shown on the graphs in appendix 8 and 9.
The five compounds tested were, apart from nos. 6, 11 and 14, two easily processed types, i.e. 80465 and a new material with low viscosity designated material X.

The graphs show the output vs screw RPM, Specific Energy Consumption vs output, and torque vs output for the 5 materials with standard screw, PVC screw and Extrucad screw.

5.6.4 Results and Comments to the Tests

Output vs screw RPM
The results are presented in appendices 8.1 to 8.2. The general trend is that for all the materials the output is highest for the Extrucad screw, about 2-3 times higher than with the traditional screws. Some measuring points are marked with a “B”. This indicates that water bubbles have been created due to overheating of the material.
For the low viscosity compound X, the improved output levels off at high rpm due to increased pressure back flow which is not observed with the high viscosity compounds.
For compound nos. 6 and 14 the increase in maximum output is approx. 200% and for no. 11 the improvement is a little lower as this compound in fact gives a better output on the older screws. For no. 14 it was necessary to adjust the temperature settings downwards to avoid formation of water bubbles.
On the graphs for compounds nos. 6 and 11, points calculated by the simulation programme have been included. For no. 6 the agreement is excellent. For compound no. 11 the agreement is only fair for simulation using the normal viscosity input. For this compound the elongational viscosity determined by the fitting program (E in table 4) is extremely high and may be due to an error. If we neglect the contribution of elongational viscosity the agreement is much better (curve marked sim.-el.visc.).

Specific Energy Consumption (SEC) vs Output
The results are presented in appendices 9.1 to 9.2. In the test runs the SEC was calculated from power consumption and in the simulations the shear stress at the barrel wall calculated by the Extrucad programme was used.
Also for the SEC there is a general trend showing that the specific energy needed to process the compounds is significantly lower with the Extrucad screw than with the standard screw and the PVC screw, typically 2-3 times lower.
Again there is a little different behaviour with compound X for which SEC increases dramatically at high output. The reason is the same as mentioned above, the high pressure flow more or less equals the drag flow and increased rpm does not increase the output very much. The energy consumption increases but not the output. For the other four compounds the observation of low SEC is consistent also at high output rates.
On the graph for 80465, which was one of the materials tested in project 1, we have indicated an SEC measurement from then, obtained on a 30 mm extruder equipped with barrier screw. The SEC was about 3 times higher than on the 63 mm extruder and concerning this point the Extrucad screw was clearly the best of the 3 screws.
In the graphs for nos. 6, 11 and 14 simulated values of SEC are included showing very good agreement with the real values measured in practice.
A comparison with the measured SEC of a PVC compound using the PVC screw shows that the HFFR processing with the new screw is in fact requiring less energy than the PVC on conventional machinery at high output and an equal amount at low output, see fig. 9.
**Fig 9. SEC vs Output**
Extrucad screw

- **PVC (PVC screw)**
- **Material 14**
- **Material 11**
- **Material 6**

Output, kg/h

**Fig 10. Torque vs Output**
Extrucad Screw

- **PVC (PVC screw)**
- **Mat.14**
- **Mat.11**
- **Mat.6**

Output, Kg/h

**Torque vs. Output**
The torques involved in the processes were calculated for the materials nos. 6, 11 and 14 with the Extrucad screw. The results are shown in fig. 10 in comparison with PVC processed with a PVC screw. Obviously the HFFR compounds, and especially no. 14, requires a high torque compared to PVC. In fact for compound no. 14 it was the maximum torque, 2200 Nm that was the rate limiting factor, see fig 10.

**Evaluation of the computer simulation method**
All the computer simulations performed which could be compared to real measurements have given good agreement with these, typically within 10-20% which is the best one could hope for. Selected typical results for compound nos. 6, 11 and 14 comparing simulated and real values are presented in table 5.
Table 5.

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<tr>
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<td>Standard</td>
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<td>34.4</td>
<td>2040</td>
<td>1619</td>
<td>162</td>
<td>163</td>
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</tbody>
</table>

5.6.5 Conclusion on Processing Tests

The computer simulation method has turned out to give very good agreement between simulated and real values obtained on the 63 mm extruder.
A new extruder screw and die system has been designed and produced based on the computer simulation. It has given excellent results in the test runs i.e. the output has increased and the specific energy consumption and maximum melt temperatures have decreased compared to normal screws.
Introduction of the new screw in the extruder will increase the productivity at least with a factor 2.

5.7 Production of Test Cables

5.7.1 Optical Test Cables

Single fibre cable
Using production parameters defined during the simulation, the single fibre optical cables (fig. 11) were produced at a speed of 120 m/min. The visual appearance of the cables was OK, but compound no. 14 had a little roughness in the surface as opposed to nos. 6 and 11 which were both very smooth.
The cables were coloured with an orange masterbatch, PE based, and the degree of mixing was tested under microscope and found OK.
The cables were produced with cold cooling water. This is not according to recommendations and in order to be sure that the mechanical properties were OK, tensile tests with samples of cable sheath were carried out.

Diameter: 3.0 mm

![Fig. 11 Single fibre cable.](image-url)

All samples had an elongation at break above 150% thereby fulfilling normal specifications for this property.
The three cable samples were tested according to IEC 332-1-C and IEC 332-3-C and they all passed the tests with a good safety margin.

Light Duty Cables
The larger optical light duty cables consist of a flammable core containing 12 fibres with a tight polyester jacket (fig. 1). Earlier IEC 332-3-C tests with 80465 as sheathing material were unsuccessful and to qualify as a standard sheathing material for optical cables the pass of this test is considered necessary. The cables were produced using roughly the same conditions as before but of course a larger die. The extrusion speed was 50-60 m/min and again the quality of the extrudates was good. The elongation at break again OK.

The IEC 332-3-C was again passed by all three materials, no. 11 with a large margin but nos. 6 and 14 with a narrow margin only. Addition of, say, 4% masterbatch containing flammable material might mean that the test will not be passed by a coloured sample. The smoke density test according to IEC 1034 was passed by all 3 samples.

5.7.1.1 Discussion of Results
The test cables were produced without problems at an increased line speed compared to normal. The visual appearance of the cables was OK. Experiences with production of long lengths are not yet available so possible problems with die build-up etc. may occur.

The mechanical properties of the extruded sheaths were OK and so the burning properties.

The improvements compared to the results of project 1 are in our opinion primarily due to the modified screw and die design, but also improvements in the processability of the compounds may play an important role. For the test cables, however, we concentrated on compounds that were not the easiest to process.

5.7.2 Test Production of Power Cable Jacket
Due to the results obtained when testing the new screw design in a 63 mm extruder, it was decided to continue the project in order to scale up the screw design to a 150 mm, 18 L/D extruder. Extruders with internal diameter in the range 120 to 1810 mm and length between 18 L/D to 24 L/D are typically used in the production of PVC cable sheathing for 500 volts to 1000 volts with 3 to 7 cores with a conductor cross section from 1.5 mm$^2$ to 16 mm$^2$.

According to information given by commercial producers of Halogen Free Flame Retarded compounds, shorter extruders (18 L/D) are preferred for the production of cable jacket.

As input data used for the computer simulation programme during the design of the new 150 mm 18 L/D screw, the required output for two different 750 volts cables were used, i.e. 3 x 1.5 mm$^2$ and 5 x 6 mm$^2$ with the goal of reach in the required output for maximum line speed in the range of 55 to 65 rpm on the screw, with 80 rpm being the maximum.

Further the design of the used extruder head and used tooling was taken into account during the computer simulation.

The previously measured flow data and compound characteristics for compound no. 11 were used during the computer simulation.

5.7.2.1 Extrusion Test Results
Compound no. 11
The temperature profile recommended by the compound supplier was used in the first extrusion trial.

Without the extruder head the required output for maximum line speed was reached at 15 rpm at the screw. At 60 rpm an output of approximately 2250 kg/hour was reached, which is far too high - four times higher than required.

After mounting the extruder head it was impossible to increase the screw rpm higher than 4 - 5. This was due to overload of the extruder. The max. amper consumption for this extruder motor is 350 Amp. With screw rpm between 4 and 5 the output is approx. 150 kg/hour.

The mass temperature of the compound was already in the second zone of the extruder above 190° C causing thermal breakdown of the compound.

Attempts to correct/reduce the mass temperature by altering the temperature settings of the extruder and screw were not successful.

5.7.2.2 Discussion of Results

It is our opinion at least three factors contributed to the failure of the attempt to scale up the screw design from the successful trials on a 63 mm extruder to a 150 mm internal diameter extruder:

1) A limitation in the computer software to deal with screw dimensions above approx. 115 mm may have been the prime reason for the lack of success.

2) Further lack of cooling efficiency of the extruder barrel.

3) Too narrow flow channels in the head caused a too high back-pressure build-up.

It is a requirement for future screw design experiments to reduce the compound output per screw rpm, in order to reduce the build-up of frictional heat and back pressure in the extruders when extruding HFFR compounds with fillers of the same type as used in compound no. 11.

5.7.2.3 Second Extrusion Trial

Due to the discouraging results of the testing of the computer designed screw described in 5.7.2.1 an older 120 mm 20 L/D single flight screw was re-designed to fit to a 120 mm 24 L/D extruder, i.e. prolonged with a new tip with a small increase of the screw core diameter (4 mm).

To use a single flight screw is very often recommended for the extrusion of Halogen Free Flame Retarded compounds by commercial producers, especially for compounds based upon the same type of filler as compound no. 11.

The temperature setting on the extruder line was in accordance with the recommendation given by the compound manufacturer. During the trial we increased the temperature 10° C in order to reduce the friction heat developed in the feeding zone of the extruder. This was done in an attempt to reduce the ampere consumption of the extruder motor as it was very close to the maximum limit for the extruder motor, and this was due to a very high compound mass temperature.

When the mass temperature of the extruded compound exceeds approx. 175 - 180° C crystal water will begin to evaporate. The generated steam will cause formation of bubbles in the compound causing a rough surface and a dramatic reduction of the mechanical properties.
When the screw revolution exceeded 10 rpm equal to an output of 80 kg/h the measured compound mass temperature was found to be 172° C and amper econsumption 290. A tendency to formation of air bubbles was seen.

The maximum screw revolution for this extruder is 60 rpm and the maximum ampere consumption of the motor is 317 ampere.

When increasing the screw revolution to 20 rpm the compound mass temperature increased to approx. 200 - 205° C and severe formation of air bubbles was seen.

Attempts to reduce the temperature increase in the compound caused by friction heat by adjusting the temperature setting on the different parts of the extruder were not succesful.

When producing cables with PVC-compounds the output required at normal extrusion line speed for this extruder line will be approx. 500 kg/h (corrected for differences in density between PVC- and HFFR-compounds).

5.7.2.4 Discussion of Results of the Second Extrusion Trial

With the single flight screw we achieved an output of approx. 80 kg/h of compound no. 11 without too severe formation of air-bubbles caused by evaporation of “crystal water” due to a too high and uncontrollable increase of compound mass temperature (heat generated by friction).

Further it was only possible to remove the screw from the extruder at the end of the trial using force.

Unfortunately the achieved output is only 15 % of the output when producing cables with standard PVC-compounds.

In order to be able to optimize the screw design for a larger diameter extruder (the design of flow cannels in the extruder head has also to be re-considered) for cable production with Halogen Free Flame Retarded compound based upon the same type of filler as compound no. 11, a number of further design - and production tests have to be carried out.

6. Environmental Evaluation of the Selected Materials
In order to make sure that the HFFR materials present no unexpected hazards to workers, users and to the environment, an environmental evaluation of the selected materials has been carried out by Jørgen Larsen from the Danish Technological Institute.

The report as a whole is included as appendix 10.

6.1 The Summary of the Environmental Evaluation

The report describes the accumulated results of a toxicological and eco-toxicological evaluation of the chemical ingredients in each material. The results from the evaluation of the different compounds are presented in both a specific matrix where the focus is on the material and in a relative matrix where the compounds are compared to PVC.

The results from the 3 eco-profile reports emphasized that no significant differences exist between the 3 selected HFFR compounds, neither from a toxicological nor eco-toxicological point of view. In this summary report, the presentation of the 3 HFFR compounds is therefore treated as one.

The specific matrix shows that the problematic elements ("the fingerprints") of the selected HFFR compounds are primarily in the production phase. The process takes place at an elevated temperature and pressure and there is thus a risk of run-away reaction with a danger of fires and explosions.

The breakdown products, when processing the material, comprise a number of acids, ketones and aldehydes with a potential for airway irritation in humans. The coupling agents might be of some concern in the work environment during compounding and manufacturing of products.

From a environmental point of view, carbon oxides, sulphur oxides, nitrogen oxides, and hydrocarbons are the important air emissions. Waste water from the polymerization will have a high BOD value and should therefore be treated before discharge to the recipient.

The energy consumption in the production of the selected HFFR compounds will differ according to the particular material but will in all circumstances be larger than for NKT's PVC no. 5313.

The material is only of minor concern in normal use.

When deposited on landfill, HFFR compounds are very slowly degraded, if degraded at all. HFFR compounds do not give rise to any serious problems in waste incineration.

From a health and environmental point of view, the problematic elements ("the fingerprints") in the life cycle of NKT's PVC no. 5313 are primarily in the production process (including the compounding and processing) and waste management. However, PVC may also constitute a problem during use in connection with unintentional fires.

Emissions of VCM (vinyl chloride monomer), EDC (ethylene dichloride) and dioxines are the most important substances to control in the production (during production of raw materials and polymerization), due to their potential large emissions and their health effects. From an environmental point of view, it is furthermore important to control releases of all chlorinated substances, including dioxines.

The material is only of minor concern in normal use. PVC does not burn by itself and has a comparatively high self ignition temperature. However, if other materials support a fire PVC will burn under the formation of e.g. carbon oxides and hydrochloric acid fumes and the soot formed at the fire may contain traces of dioxines, the amount depends on the fire conditions.
It is questioned for the time being whether it is feasible to recycle PVC containing lead from old cables because it keeps lead in circulation in society instead of phasing it out.

When deposited on landfill, PVC is very slowly degraded, if degraded at all. PVC plasticizer may leach out of the product and could be a source to emissions to soil and water.

By the incineration of PVC, hydrochloric acid is formed. Because of the environmental effects of the acidic fumes the stack gasses are normally neutralized by the use of large amounts of lime. Dioxines may occur, however, the amount depends on the fire conditions.

The residues from the cleaning of stack fumes from incineration of cable waste contain metals and traces of dioxines.

Even through the energy consumption during production of raw materials of the HFFR are larger than for the PVC material, the HFFR compounds must be considered as an environmentally friendly alternative to PVC. This judgement is primarily based on the fact that no potential for exposure and effects of carcinogenic substances during production and lower amounts of acidic fumes and dioxines are formed by waste disposal. Furthermore, there is no need for addition of plasticizers like e.g. phthalates often used in products made of PVC. The material is only of minor concern in normal use, however, PVC may constitute a problem during use in connection with unintentional fires. If other materials support a fire PVC will burn under the formation of e.g. carbon oxides and hydrochloric acid fumes. The soot formed at the fire may contain traces of dioxines, dependent on the fire conditions.
7. Status for Halogen Free Materials for Cables

The barriers towards the increased use of HFFR materials in cables have been reduced but not yet eliminated. For environmental and safety reasons the customers are increasingly asking for halogen free cables. This leads the suppliers of these materials to develop more and more competitive compounds, price wise and quality wise.

In this project it has been demonstrated that compounds exist which fulfil requirements for nearly all properties, except the flexibility requirement for flexible cords where improvements are still needed.

The universal material with optimum properties in every respect has not yet been developed. But ways have been found to improve water resistance, oil resistance, UV resistance and processability to acceptable levels.

The final step will be to combine the advantages into one single compound, but this will probably take some years to develop if possible at all.

The project has shown that significant improvements in processing can be obtained during the production of optical cable by adjusting the design of the screw and other extruder tools.

DRAKA-NKT is the first within the Danish cable industry who has a standard range of optical data cables based upon halogen free materials. In the autumn of 1995 NKT Cables presented a range of power cables based upon HFFR materials.
8. Conclusion

Sixteen HFFR materials have been tested for short and long term properties.

Significant improvements compared to previously tested materials have been observed.

Some materials have been found with extremely good properties in one respect and very poor in another and some with acceptable but not extremely good properties in all respects.

The tests also show that the best materials have properties which are comparable with those of PVC with regard to dry and wet ageing, oil resistance, and UV resistance. This means that if they are tested and selected properly the HFFR materials can be used in environments that were not considered previously such as in buried cables, with oil contact at moderate temperatures and exposed to sunlight (if stabilized properly).

Tests of two cross linked compounds showed no significant advantage.

The processing properties of some of the tested materials were very good but unfortunately these easy processing types had serious drawbacks in other respects like burning properties which are of great importance.

For the high viscosity types that were more difficult to process significant process improvements (line speed) have been achieved during the production of optical cables by adjusting screw and die geometry. The improvements have been verified by the production of test cables with excellent properties.

The adjustments were based on computer simulation of the extrusion process with HFFR materials thoroughly characterized by rheological measurements. The agreement between values from the computer simulation and values measured on the cable production extruder was acceptable.

The positive effect of mixing elements in the extruder screw has been demonstrated.

The results of the project is or will be implemented in the production of optical cables.

Concerning the possibilities of increasing the line speed during the production of installation- and power cables further development work have to be carried out.

Improvement of the design of the extruder screws and head toolings have to be accomplished or lower production speed than for cables based upon PVC compound have to be accepted. Which will require capital intensive investments in new production lines if the same production output shall be achieved.

As a result of the environmental evaluation, the HFFR compounds must be considered as an environmental friendly alternative to PVC.
Appendix 1 ............... Dry Ageing Tests
Appendix 2 ............... Ageing in water pH 7
Appendix 3 ............... Ageing in water pH 4
Appendix 4 ............... Ageing in oil
Appendix 5 ............... Ageing in Cable Vaseline
Appendix 6 ............... UV Ageing Tests
Appendix 7 .............. Mixing Experiments

Appendix 8 .............. Extrusion Tests
Output vs. screw RPM

Appendix 1 .............. Dry Ageing Tests

Material 1. Dry ageing.

Material 3. Dry ageing.
Material 2. Dry ageing.

![Graph showing elongation and tensile strength over time for Material 2.](image)

Material 4. Dry ageing.

![Graph showing elongation and tensile strength over time for Material 4.](image)
Material 5. Dry ageing.

Material 6. Dry ageing.

Material 7. Dry ageing.
Appendix 10.24

Material 15. Dry ageing.

PVC material. Dry ageing.

Material 1. Ageing in water pH7

Material 1. Ageing in water pH7
### Material 8. Ageing in water pH7

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### Material 9. Ageing in water pH7

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Material 14. Ageing in water pH7

Material 15. Ageing in water pH7

Material 15. Ageing in water pH7

Material 15. Ageing in water pH7

Appendix 10.31
Appendix 3: Ageing in water pH4

Material 1. Ageing in water pH4

- Weight change [%]
- Tensile strength [MPa]
- Elongation at break [%]

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</table>
Material 2. Ageing in water pH4

- Weight change [%] vs Time [weeks]
- Tensile strength [MPa] vs Time [weeks]
- Elongation at break [%] vs Time [weeks]

Material 3. Ageing in water pH4

- Weight change [%] vs Time [weeks]
- Tensile strength [MPa] vs Time [weeks]
- Elongation at break [%] vs Time [weeks]
Material 8. Ageing in water pH4

Material 9. Ageing in water pH4
Material 10. Ageing in water pH4

Material 11. Ageing in water pH4
Material 12. Ageing in water pH4

Material 13. Ageing in water pH4
### Material 14. Ageing in water pH4

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### Material 15. Ageing in water pH4

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<th>Time [weeks]</th>
<th>Weight change [%]</th>
<th>Tensile strength [MPa]</th>
<th>Elongation at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix 4: Ageing in oil (ASTM no. 2)

Material 1. Ageing in oil (ASTM no. 2)

- Weight change [%]
  - 0 10 20 30 40 50
  - Temperature: 20°, 80°, 100°

- Tensile strength [MPa]
  - 0 10 20 30 40 50
  - Temperature: 20°, 80°, 100°

- Elongation at break [%]
  - 0 10 20 30 40 50
  - Temperature: 20°, 80°, 100°
### Material 2. Ageing in oil (ASTM no. 2)

<table>
<thead>
<tr>
<th>Time [weeks]</th>
<th>Weight change [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°</td>
</tr>
<tr>
<td></td>
<td>50°</td>
</tr>
<tr>
<td></td>
<td>80°</td>
</tr>
<tr>
<td></td>
<td>100°</td>
</tr>
</tbody>
</table>

### Material 3. Ageing in oil (ASTM no. 2)

<table>
<thead>
<tr>
<th>Time [weeks]</th>
<th>Tensile strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°</td>
</tr>
<tr>
<td></td>
<td>50°</td>
</tr>
<tr>
<td></td>
<td>80°</td>
</tr>
</tbody>
</table>

### Material 3. Ageing in oil (ASTM no. 2)

<table>
<thead>
<tr>
<th>Time [weeks]</th>
<th>Elongation at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°</td>
</tr>
<tr>
<td></td>
<td>50°</td>
</tr>
<tr>
<td></td>
<td>80°</td>
</tr>
</tbody>
</table>
Material 6. Ageing in oil (ASTM no. 2)

Material 7. Ageing in oil (ASTM no. 2)
Material 8. Ageing in oil (ASTM no. 2)

Material 9. Ageing in oil (ASTM no. 2)
### Material 10. Ageing in oil (ASTM no. 2)

<table>
<thead>
<tr>
<th>Time [weeks]</th>
<th>20°C</th>
<th>50°C</th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight change [%]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>

### Material 11. Ageing in oil (ASTM no. 2)

<table>
<thead>
<tr>
<th>Time [weeks]</th>
<th>20°C</th>
<th>50°C</th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight change [%]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

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---
Material 12. Ageing in oil (ASTM no. 2)

Weight change [%]

20° 50° 80° 100°

Material 13. Ageing in oil (ASTM no. 2)

Elongation at break [%]

20° 50°
Material 14. Ageing in oil (ASTM no. 2)

Material 15. Ageing in oil (ASTM no. 2)
Material 16. Ageing in oil (ASTM no. 2)

- Weight change [%] vs. Time [weeks]
- Tensile strength [MPa] vs. Time [weeks]
- Elongation at break [%] vs. Time [weeks]

PVC material. Ageing in oil (ASTM no. 2)

- Weight change [%] vs. Time [weeks]
- Tensile strength [MPa] vs. Time [weeks]
- Elongation at break [%] vs. Time [weeks]
Material 6, cured and uncured.
Ageing in oil (ASTM no. 2)

Material 17. Ageing in oil (ASTM no. 2)
Appendix 5: Ageing in Vaselin

Material 6. Ageing in Vaselin

![Graph showing weight change over time for different temperatures.]

- Weight change [%]
- Time [weeks]
- Temperatures: 20°, 50°, 80°

![Graph showing tensile strength over time for different temperatures.]

- Tensile strength [MPa]
- Time [weeks]
- Temperatures: 20°, 50°

![Graph showing elongation at break over time for different temperatures.]

- Elongation at break [%]
- Time [weeks]
- Temperatures: 20°, 50°

- **Weight change [%]**
  - **Temperature [°C]**: 20, 50, 80
  - **Time [weeks]**: 0, 10, 20, 30, 40, 50

- **Tensile strength [MPa]**
  - **Temperature [°C]**: 20, 50, 80
  - **Time [weeks]**: 0, 10, 20, 30, 40, 50

- **Elongation at break [%]**
  - **Temperature [°C]**: 20, 50, 80
  - **Time [weeks]**: 0, 10, 20, 30, 40, 50
Appendix 6: UV ageing

Material 1 to 5. UV ageing

Material 6 to 10. UV ageing

Material 11 to 15. UV ageing
Appendix 7:

7.1 Mixing obtained with screw design 1

7.2 Mixing obtained with screw design 2
Appendix 8: Output vs. RPM

Output vs rpm
Material 6

Output vs rpm
Material 11

Output vs rpm
Material 14
Appendix 10.57

Output vs rpm

Material X

- Standard screw
- PVC screw
- Extrucad screw

Output vs rpm

- Standard screw
- PVC screw
- Extrucad screw
Appendix 10:

Environmental aspects of selected compounds for cable production

Prepared by
Jørgen Larsen

Danish Technological Institute
Centre of Environmental Technology

June 1996
# Table of Contents

1. Introduction

2. Summary of the report

3. Method
   3.1 Eco-profiles
      3.1.1 Description of the elements used to assess the health and environmental impacts of the selected compounds.

   3.2 Presentation of the results

4. Assessment of the selected compounds
   4.1 Summary/remarks of the assessment of NKT’s PVC
   4.2 Summary/remarks of the assessment of the HFFR compounds

5. Conclusion/comparison

Reference
1. Introduction

This report is a study of the environmental and health aspects related to different plastics used as materials for cable production. DRAKA/NKT has during the last couple of years performed extensive investigations of selected HFFR compounds on the market. Since the aim of this work is to improve the environment by substituting PVC used for cable production with HFFR compounds the Danish Technological Institute, Department of Environmental Technology, has performed a toxicological (health aspects) and eco-toxicological assessment (effects on the external environment) of the 3 finally selected HFFR compounds

- Compound no. 11
- Compound no. 6
- Compound no. 14

and made a comparison of the selected compounds to the NKT's PVC compound no. 5313 presently used for cable production.

In the evaluation of the materials, an eco-profile has been made for each material. The aim of these eco-profiles is to provide clear and transparent information on the potential impacts of the material on health/environment and to identify if any problematic elements ("the fingerprint") of that particular material are present.

During the preparation of an eco-profile report, it is absolutely necessary to know the exact composition of the product. All firms involved have provided the exact composition details of their products to the consultants which makes it possible to prepare four eco-profile reports, one for each of the products (the 3 selected HFFR compounds and the NKT's PVC). As the exact composition details of these products are highly confidential it is not possible to publish the information in this report. Therefore, the report only includes a short summary of the main conclusions and not the exact information about
e.g. the consumption of energy and raw materials for the production of the different materials (the information can only be found in the eco-profile reports prepared for each material). Thus, the present report is only a part of a larger reporting complex on "integrated environmental and occupational assessment of selected plastics used in connection with cable production."
2. Summary of the report

The report describes the accumulated results of a toxicological and eco-toxicological evaluation of the chemical ingredients in each material.

The results from the evaluation of the different compounds are presented in both a specific matrix where the focus is on the material and in a relative matrix where the compounds are compared to PVC.

**HFFR compounds**

The results from the 3 eco-profile reports emphasized that no significant differences exist between the 3 selected HFFR compounds, neither from a toxicological nor eco-toxicological point of view. In this summary report, the presentation of the 3 HFFR compounds is therefore treated as one.

The specific matrix shows that the problematic elements (“the fingerprints”) of the selected LSOH compounds are primarily in the production phase. The process takes place at an elevated temperature and pressure and there is thus a risk of run-away reaction with a danger of fires and explosions.

The breakdown products, when processing the material, comprise a number of acids, ketones and aldehydes with a potential for airway irritation in humans. The coupling agents might be of some concern in the work environment during compounding and manufacturing of products.

From a environmental point of view, carbon oxides, sulphur oxides, nitrogen oxides, and hydrocarbons are the important air emissions. Waste water from the polymerization will have a high BOD value and should therefore be treated before discharge to the recipient.

The energy consumption in the production of the selected HFFR compounds will differ according
to the particular material but will in all circum-
stances be larger than for NKT’s PVC no. 5313.

The material is only of minor concern in normal
use.

When deposited on landfill, HFFR compounds
are very slowly degraded, if degraded at all.
HFFR compounds do not give rise to any serious
problems in waste incineration.

**NKT’s PVC no. 5313**

From a health and environmental point of view,
the problematic elements ("the fingerprints") in
the life cycle of NKT’s PVC no. 5313 are
primarily in the production process (including the
compounding and processing) and waste
management. However, PVC may also constitu-
tate a problem during use in connection with
unintentional fires.

Emissions of VCM (vinyl chloride monomer),
EDC (ethylene dichloride) and dioxines are the
most important substances to control in the
production (during production of raw materials
and polymerization), due to their potential large
emissions and their health effects. From an
environmental point of view, it is furthermore
important to control releases of all chlorinated
substances, including dioxines.

The plasticizers might perhaps be of some
concern in the work environment during
compounding and manufacturing of products.

The material is only of minor concern in normal
use. PVC does not burn by itself and has a
comparatively high self ignition temperature.
However, if other materials support a fire PVC
will burn under the formation of e.g. carbon oxi-
des and hydrochloric acid fumes and the soot
formed at the fire may contain traces of
dioxines, the amount depends on the fire con-
ditions.

It is questioned for the time being whether it is
feasible to recycle PVC containing lead from old
cables because it keeps lead in circulation in
society instead of phasing it out.

When deposited on landfill, PVC is very slowly
degraded, if degraded at all. PVC plasticizer
may leach out of the product and could be a source to emissions to soil and water.

By the incineration of PVC, hydrochloric acid is formed. Because of the environmental effects of the acidic fumes the stack gasses are normally neutralized by the use of large amounts of lime. Dioxines may occur, however, the amount depends on the fire conditions.

The residues from the cleaning of stack fumes from incineration of cable waste contain metals and traces of dioxines.

**Relative matrix**

Even through the energy consumption during production of raw materials of the HFFR are larger than for the PVC material, the HFFR compounds must be considered as an environmentally friendly alternative to PVC. This judgement is primarily based on the fact that no potential for exposure and effects of carcinogenic substances during production and lower amounts of acidic fumes and dioxines are formed by waste disposal. Furthermore, there is no need for addition of plasticizers like e.g. phthalates often used in products made of PVC. The material is only of minor concern in normal use, however, PVC may constitute a problem during use in connection with unintentional fires. If other materials support a fire PVC will burn under the formation of e.g. carbon oxides and hydrochloric acid fumes. The soot formed at the fire may contain traces of dioxines, dependent on the fire conditions.
3. Method

3.1 Eco-profiles

For each of the selected compounds, an eco-profile has been made. An eco-profile describes the health and environmental impacts of the material through production of raw material, production, use and waste management. The aim of these eco-profiles is to give information on the potential impacts of the material on health and environment. Thus, an eco-profile is able to identify if there are any problematic elements ("the fingerprint") of each single material.

The chapters in each eco-profile report follow the phases in the life cycle of the material: production of raw materials and polymerization, compounding and processing, use, and waste management.

It should be mentioned explicitly that during production of raw materials and polymerization, the focus has been made on the polymer while the different additives (including the consumption of energy during production of raw materials for the filler) are evaluated during compounding and processing. The evaluation of additives is based on screening for potential health and environmental effects (hazard assessment).

Eco-profiles take into account material and energy inputs and outputs in the form of emissions to land, air, and water. They do not pretend to be a full-scale life cycle assessment methodology but a screening of the potential impact of a particular material on health and environment and can provide the raw data on which LCA studies on products can be based.

3.1.1 Description of the elements used to assess the health and environmental impacts of the selected compounds.

The eco-profile reports describe the compounds through of the following phases
· production of raw materials and polymerization,
· compounding and processing,
· use, and
· waste management

For each of the phases a number of environmental elements are discussed:

· consumption of raw materials, energy and the related emissions
· waste and recycling
· screening for potential health effects
· screening for potential environmental effects
· accidents

The procedure and terminology of these reports have been kept as close as possible to the international development, particularly EU-classification of substances and the work related to SETAC (Society of Environmental Toxicology and Chemistry).

3.2 Presentation of the results

The present report is therefore a summary of a larger reporting complex. Four eco-profile reports, one for each of the 3 selected HFFR compounds and one for NKT's PVC no. 5313 have been made.

The results of this assessment are displayed in both a specific matrix, where the focus is on the material, and in a relative matrix where the compounds are compared to PVC no. 5313 (stabilized with calcium-zinc stabilizers and without the use of chlorinated paraffins). In the specific matrix, each element is graded following a three-step scale

· problematic
· potentially of some concern, and
· no or only minor concern.

In the relative matrix, the 3 selected compounds are compared in each element using a scaling from much worse than PVC to much better than PVC.
4. Assessment of the selected compounds

4.1 Summary/remarks of the assessment of NKT’s PVC

In 1993, NKT started to market cables stabilized with calcium-zinc stabilizers instead of lead and without the use of chlorinated paraffins. This evaluation is based on this "new" PVC material no. 5313. The results of this assessment are displayed in a specific matrix, as can be seen in the table below.

From a health and environmental point of view, the problematic elements ("the fingerprints") in the life cycle of PVC are primarily in the production process (including the compounding and processing) and waste management. However, PVC may also constitute a problem during use in connection with unintentional fires.

<table>
<thead>
<tr>
<th></th>
<th>Consumption of energy and resources</th>
<th>Work environment</th>
<th>External environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production of raw materials &amp; polymerization</td>
<td>0</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Compounding and processing</td>
<td>0</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Use</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Waste management(^2)</td>
<td>?</td>
<td>0</td>
<td>+++</td>
</tr>
</tbody>
</table>

+++ problematic
+ potentially some concern
0 no or only minor concern
? no information

Note
(1) By combustion in fires, PVC may form HCl and dibenzo-p-dioxins.
(2) After having used the cable product, which has an expected lifetime of at least 20 years.
Table no 1  
Specific assessment of NKT's PVC no 5313

| Production of raw material & polymerization | Emissions of VCM (vinyl chloride monomer), EDC (ethylene dichloride) and dioxines are the most important substances to control in the production of VCM and PVC, due to their potential large emissions and their health effects. Dioxines are very acute toxic (Ahlborg et al., 1988) while VCM and EDC are classified as toxic and carcinogenic (EU and IARC, 1987). Hydrogen chloride is a corrosive colourless gas which is classified as corrosive and it is very irritating for mucous membranes. From an environmental point of view, it is further important to control releases of all chlorinated substances, including dioxines. The degradation of dioxines in soil is minimal, the substance must be considered as having a high bioaccumulation potential and being highly toxic (Christiansen et al. 1990). The average consumption of energy for the production of 1 kg of PVC is about 67 MJ over all the polymerization processes (Bounstad, 1994). |
| Compounding and processing | In the compounding process, raw PVC is mixed with a number of additives. The additives used with NKT's PVC being fillers, plasticizers, and heat stabilizers. The effects of VCM and hydrogen chloride described under production of raw materials and polymerization are also valid for this phase. However, the exposure is, in this phase, considerable less. In the work environment, the filler may cause some irritation and may be hazardous as dust but it is not acute toxic. In the external environment, the filler may cause some temporary damage to local plant during production. However, it is not classified as dangerous to the environment. |
Compared with most other normally used stabilizers, the stabilizers used in this material are fairly non-toxic in the work environment.

It is also reported to be relative harmless in the terrestrial environment but one of them may cause acute toxicity in the aquatic environment (Merian E., 1991, Friberg L. et al. 1986, Seiler H. & Sigel H., 1988).

From a toxicological and eco-toxicological point of view, the effects of these substances are less problematic than lead which has been used, previously.

The plasticizers might perhaps be of some concern in the work environment during compounding and manufacturing of products. The plasticizers might be carcinogenic to humans and might have a xenoestrogenic effects Møller, S. et al., 1995). The plasticizer does not seem to be acute toxic to aquatic organisms. However, it may exhibit chronic toxicity and may cause long-term adverse effects in the aquatic environment. Due to low biodegradability at low temperatures and in unacclimated systems, the plasticizer may accumulate in sediments and soils in areas where temperatures are relatively low.

Use

The material is only of minor concern in normal use. The filler and stabilizer are locked into the PVC matrix but plasticizer loss may occur. However, the plasticizer which is released to the environment is not expected to cause acute toxic effects in neither the aquatic nor the terrestrial environment but since anaerobic degradation is very slow accumulation may occur in low-oxygenated areas in the environment.

PVC does not burn by itself and has a comparatively high self ignition temperature. However, if other materials support a fire PVC will burn under the formation of e.g. carbon
oxides and hydrochloric acid fumes. The hydrochloric acid is very irritative to the respiratory system and corrosive to buildings, especially electronic equipment. The soot formed at the fire may contain traces of dioxines, dependent on the fire conditions.

**Waste management**

When deposited on landfill, PVC is degraded very slowly, if at all. PVC plasticizer may leach out of the product (Malme, 1994) and this could be a source to emissions to soil and water.

Largely, all PVC production waste from cable production can be recycled. For the time being, it is questioned whether it is feasible to recycle PVC from old cables. The reason is partly problems with sorting, partly poor material quality in the often very old cables.

By the incineration of PVC, hydrochloric acid is formed. Because of the environmental effects of the acidic fumes the stack gases are normally neutralized by the use of large amounts of lime (Hjalmar, Thomassen, Højmark, 1990 and Rasmussen, 1995). However, NKT has forwarded a patent application for a process which will solve this situation.

The residues from the cleaning of stack fumes from incineration of cable waste contain metals and traces of dioxines. It is necessary to deposit those hazardous residues under controlled conditions and with constant collection and treatment of the leachate.

In Denmark, recycling plants with an approved method to treat old cable waste do exist. However, it is expected that incineration of cable insulation with copper, to a certain extent, takes place in open fires in order to recycle the copper. It is not possible to estimate to what extent this is done.
4.2 Summary/remarks of the assessment of the HFFR compounds

The problematic elements ("the fingerprints") in the life cycle of the HFFR compounds is primarily the production process. This process takes place at an elevated temperature and pressure and there is thus a risk of run-away reaction with a danger of fires and explosions.

The energy consumption in the production of the HFFR compounds will differ according to the quality of the compounds but will in all circumstances be significantly larger than for PVC compound.
Consumption of energy and resources | Work environment | External environment
--- | --- | ---
Production of raw materials & polymerization | + | + | +
Compounding and processing | 0 | ? | 0
Use | 0 | 0 | 0
Waste management | ? | 0 | +

+++ problematic
+ potentially some concern
0 no or only minor concern
? not sufficient information, but may be of some concern

Note
(1) It is assumed that HFFR compounds can be recycled, however, the possibility of recycling HFFR has not yet been demonstrated.

Table no 2
Specific assessment of HFFR compounds

Production of raw material & polymerization

The health effects related to the processing of the selected HFFR compounds are often connected to groups of ingredients instead of single compounds. The production processes are to a great extent closed processes. Emissions of aerosols from a number of acids, ketones and aldehydes are the most important substances to control, these have a potential for airway irritation. In the case of long-term exposure there may be a risk of more chronic effects like a decrease in lung function. Work environment effects in the HFFR processing industry is primary respiratory tract effects.

From an environmental point of view, carbon oxides, sulphur oxides, nitrogen oxides and hydrocarbons are important air emissions. Waste water from the polymerization will
contain some oil emulsions, hydrocarbons, dissolved organic materials and residues from various process chemicals. These emissions have a high BOD (Biological Oxygen Demand) value and the waste water should be treated before discharge to the recipient.

**Compounding and processing** In processes involving heating, thermic degradation might occur. The health and environmental effects would be the same as described during production of raw material and polymerization. No serious toxic effects during normal compounding and processing of HFFR compounds are expected. However, the coupling agents might perhaps be of some concern in the work environment during compounding and manufacturing of products.

**Use** The material is only of minor concern in normal use. The filler and stabilizer are locked into the polymer matrix and no environmental effects are expected. The raw materials are relatively harmless in the external environment. A potential exposure to materials and degradation products is supposed to be so slight that the effects are negligible.

The polymer in these compounds may acts as a fire promoter, however, some of the additives are used as synergistic flame-retardants. If other materials support a fire the HFFR compounds will burn under the formation of e.g. carbon oxides and polycyclic aromatic hydrocarbons. The inorganic additives will be found in the ashes but is not expected to have any toxic effects.

**Waste management** The exposure to and the effects on the work environment in relation to waste disposal are not known but they are supposed to be negligible. It is questioned for the time being whether it is feasible to recycle HFFR compounds from old cables. The reason is partly problems with sorting, partly poor material quality.
When deposited on landfill HFFR compounds are very slowly degraded, if degraded at all.

HFFR compounds do not give rise to any serious problems in waste incineration. The total combustion of HFFR compounds mainly yields carbon dioxide, water, carbon monoxide, soot, polycyclic aromatic hydrocarbons (PAH), and ashes containing inorganic materials with a relative low toxicity.
5. Conclusion/comparison

The discussion of the substitution of PVC in cables involves a number of relevant issues such as an evaluation of the effects of chlorinated substances, including dioxines. Not least in recent years, the focus has also been on the additives in PVC. The toxicological and eco-toxicological concern applies, in particular, to lead stabilizing agents, phthalate plasticizers and chloroparaffins. These have all been used in cables, however, in 1993, NKT started to market cables stabilized with calcium-zinc stabilizers instead of lead and without the use of chlorinated paraffins. This evaluation and comparison of possible alternatives (the 3 selected HFFR compounds) is based on the "new" NKT PVC compound no. 5313.

The energy consumption is estimated as being significantly larger for HFFR than for PVC. However, the HFFR compounds must be considered as an environmentally friendly alternative to PVC. This judgement is primarily based on the fact that no carcinogenic substances are released during production. Furthermore, there is no need for addition of plasticizers like eg. phthalates normally used in compounds made of PVC in connection with cable production.

The potential risk for accidents might be fewer in the production of HFFR due to the use of chlorine in the PVC production and the possibility of the formation of corrosive compounds in fires. However, because of the high temperature and pressure in the process production of HFFR, it is considered to have the same potential for impact as the production of PVC.

Furthermore, PVC may constitute a problem during use in connection with unintentional fires.
If other materials support a fire PVC will burn under the formation of e.g. carbon oxides and hydrochloric acid fumes. The hydrochloric acid is very irritative to the respiratory system and corrosive to buildings, especially electronic equipment. The soot formed at the fire may contain traces of dioxines, dependent on the fire conditions.

HFFR compounds also result in fewer problems in the waste disposal than PVC due to the lower content of problematic additives and the lower chlorine content. Thus, lower amounts of acidic fumes and dioxines are formed by waste incineration.

Thus, the production of HFFR results in the same or in fewer problems in the work environment and external environment than NKT’s PVC through the entire life cycle.
### Table no 3

**Relative assessment of HFFR compounds in relation to PVC**

<table>
<thead>
<tr>
<th></th>
<th>Consumption of energy and resources</th>
<th>Work environment</th>
<th>External environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production of raw materials &amp; polymerization</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Compounding and processing</td>
<td>-</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>Use</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Waste management</td>
<td>?</td>
<td>0</td>
<td>+++²</td>
</tr>
</tbody>
</table>

+++ potentially much less impact than PVC  
+ potentially less impact than PVC  
0 approximately the same impact as PVC  
- potentially greater impact than PVC  
--- potentially much greater impact than PVC

**Note**

(1) By combustion in fires, PVC may form HCl and dibenzo-p-dioxins.  
(2) This evaluation is based on the possibility of recycling HFFR, however, it has not yet been demonstrated.
Reference


