Material Identity Card

Survey of Materials for Transmission Line Equipment and Identification Methods

Technical Report

Material Identity Card

Survey of Materials for Transmission Line Equipment and Identification Methods

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PRODUCT DESCRIPTION

Long-term optimization of transmission lines in the service environment requires control of the quality of products used in network components. Quality assessment of materials, both during manufacture and in the service environment, is at present based on expensive testing techniques. Electricité de France (EDF) has developed an alternative to conventional testing techniques. EDF's Materials Identity Card (MIC) approach to material assessment focuses on the materials in cables and synthetically insulated accessories. This approach "fingerprints" all relevant materials and gives a higher priority to dossier analysis (existing dossiers, experience feedback, structural-property relationships) than to conventional tests.

Results & Findings

A general method of identifying materials has been developed as an organization chart from which important structural-property relationships of materials in cables and synthetically insulated accessories can be accessed. This report includes that organization chart. Case studies also are discussed and a directory of cable and accessory manufacturers provided.

Challenges & Objectives

To insure long-term optimization of transmission lines in the service environment, several objectives must be met:

- eliminate drift over time in materials formulation
- identify chemical changes in formulations proposed by manufacturers and suppliers
- verify the chemical nature of products damaged when operating incidents occur and/or during qualification campaigns

MIC will assist EDF in meeting these objectives and, in the process, help reduce the costs of both qualifying and performing quality control on cable materials and synthetically insulated accessories.

Applications, Values & Use

MIC focuses on structural-property relationships of materials in cables and synthetically insulated accessories. Information accessed from MIC can be used to create "fingerprints" for these materials, which, in turn, can simplify procedures for qualifying and assessing drift in formulation over time (caused by manufacturer/suppliers or by in-service material deterioration).

EPRI Perspective

Structural parameters of transmission line equipment—accessible by means of existing characterization techniques—that can influence material properties have been identified. In practice, analysis of materials after formulation is not always easy since interpretation can be tenuous due to the presence of fillers. This difficulty highlights the need to collaborate with manufacturers and suppliers of raw materials to access all structural parameters.

This study shows that morphology is a key parameter influencing electrical properties. This observation highlights the need to determine the fraction of free volume in materials. How to make this determination requires further study.

Approach

The project team initiated this program by observing that material structural parameters for transmission line equipment were already available from manufacturers. The team proposed using this information to develop a dynamic database that would enable conclusions to be drawn relating to the influence modifications in structural parameters have on material properties. The core of the team's database was the Quantitative Structure Property Relationship (QSPR) mathematical tool. By compiling manufacturer data into QSPR, the team was able to generate mathematical relationships between descriptors and properties. Using actual case studies, based on manufacturers' proposals, the team was able to validate the tool.

Keywords

Materials identity card
Quantitative structure property relationship
Materials fingerprint
Transmission cable materials

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1

INTRODUCTION

The long-term optimization of transmission lines in the service environment requires control of the quality of the products used in network components. Requirements are as follows:

- no drift over time in the formulation of the materials delivered
- identification of chemical changes in the formulations proposed by manufacturers/suppliers
- verification of the chemical nature of the products damaged when operating incidents occur and/or during qualification campaigns

Quality assessment of the material, both initially and in the course of its use in the service environment, is at present based on testing techniques, with attendant high costs.

The purpose of the “Materials Identity Card” approach (MIC) is to focus on the materials making up the cables and synthetically insulated accessories, and hence:

- to simplify procedures for qualification and expert assessment when drift in formulation over time occurs (caused by manufacturer/suppliers, or by deterioration of the materials in service conditions), therefore make a “fingerprint” of the material
- secondly to give higher priority to **dossier analysis** (existing dossiers, experience feedback, structural – property relationships) than to tests

This approach should enable EDF to reduce the cost of the qualification and of the quality control of cable materials and synthetically insulated accessories.

2

PURPOSE OF THE STUDY

One way of meeting our general purpose would have been to collect all the results from the many evaluations of cables and accessories in the last thirty years, and put them in a materials database. The disadvantage of this approach is that it is static, and relates only to fixed cases. The approach adopted was therefore more dynamic, and mainly based on the establishment of structural/property relationships (either empirical or database generated). This approach requires a precise knowledge of the structures of materials.

The approach is shown in Figure 2-1, which shows that the tests to identify properties at the time (following a change in material or for assessment purposes) are no longer necessary, if replaced by a Materials Identity Card which is less costly in terms of testing, and relies on the identification of structure/property relationships.

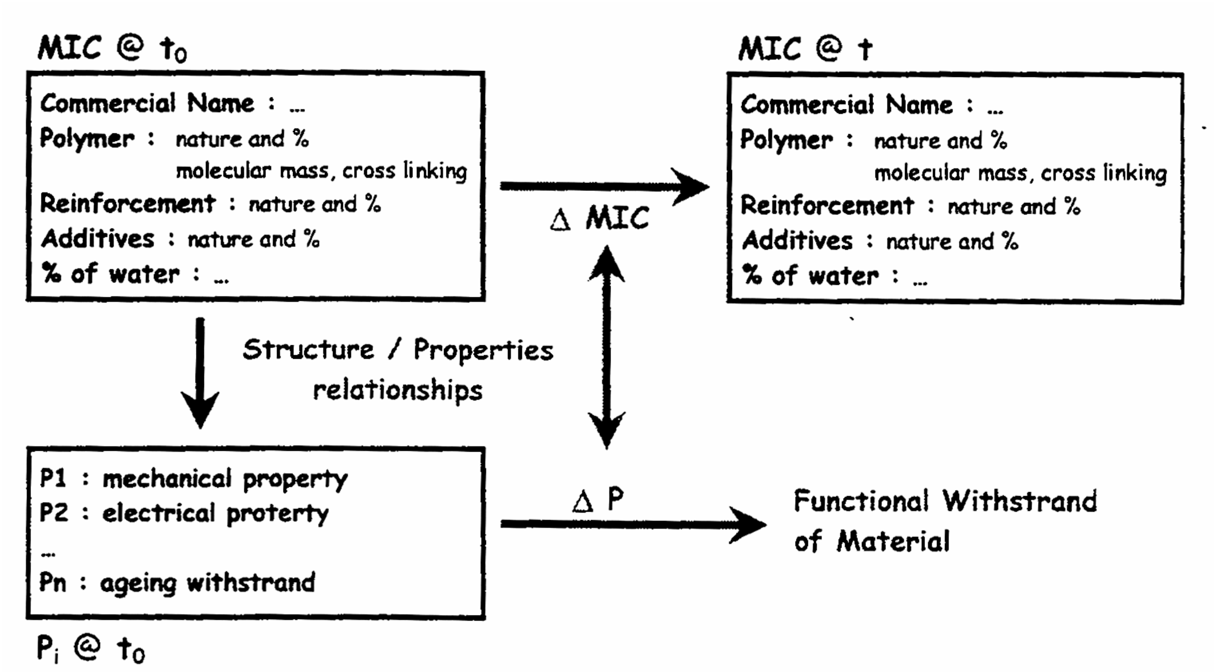

Figure 2-1
Schematic of Overall "Material Identity Card" (MIC) Approach

The various stages to achieving our final objective were as follows:

1. Surveying materials in use.

2. Physical and chemical characterization of the materials and creating the MIC.

3. Establishing structural/property relationships.

4. Determining the critical structural parameters required for acceptable structural withstand (i.e., establishing a relationship between the changes in the MIC and in the functional withstand of the materials).

The present report relates to the completion of the **first 2 stages**, which led to the development of the "Materials Identity Card" tool identifying materials composition.

The first stage was to survey the materials customarily compounded into cables and synthetic accessories, and make an assessment of the diversity of the materials, their constituents, and the manufacturers and suppliers of the raw materials. After this first phase, a number of case studies were selected.

In the second stage, the physical and chemical characterizations implemented in the selected case studies were described. The study of the benefits and limitations of each type of test made it possible to build up the toolbox of methods of characterization, taking into account the information level required for a proper understanding of the composition of the materials used. If the physical and chemical analyses were to be properly interpreted, a summary bibliography of the constituent materials used was necessary.

Finally, based on the initial results of the case studies, a general methodology could be envisioned.

Once the study is completed, a modular approach will be presented for discussion, taking into full account the transmission line system studied. On completion, this first stage gave rise to an evaluation of the circumstances in which a materials study based approach might be appropriate. At the same time, other circumstances were identified in which the limitations of this method became apparent.

3

DESCRIPTION OF COMPONENTS

The contour of the study was limited to materials used for HTB medium voltage transmission lines (63 kV to 400 kV).

3.1 Cables

Cable configuration depends on the voltage range of the transmission line in service.
The components covered by the study were:

- the jacket (or oversheath)
- the insulation
- the semi-conductive shields (or screens)

Higher service stress levels in HTB cables imply higher quality insulation and sheaths. It is particularly important that the materials are perfectly clean, as their long-term behavior may be substantially influenced by micro-impurities. Purity precautions must be taken both in manufacturing phase for raw materials, and in the cable manufacturing process. Synthetic insulation materials when subject to high voltage stress are sensitive to humidity. It is therefore essential to avoid any contact with water or water vapor during the manufacturing process and when the line is in operation. This is the role of the jacket (or oversheath), and of the watertight metal sheath (which also serves as a screen).

The function of the internal semi-conductive shield is to homogenize the potential of the electrical field to the potential of the core, whereas in the outer semi-conductive shield, the potential is zero.

Figure 3-1 shows in detail the internal structure of a synthetically insulated 400 kV cable.

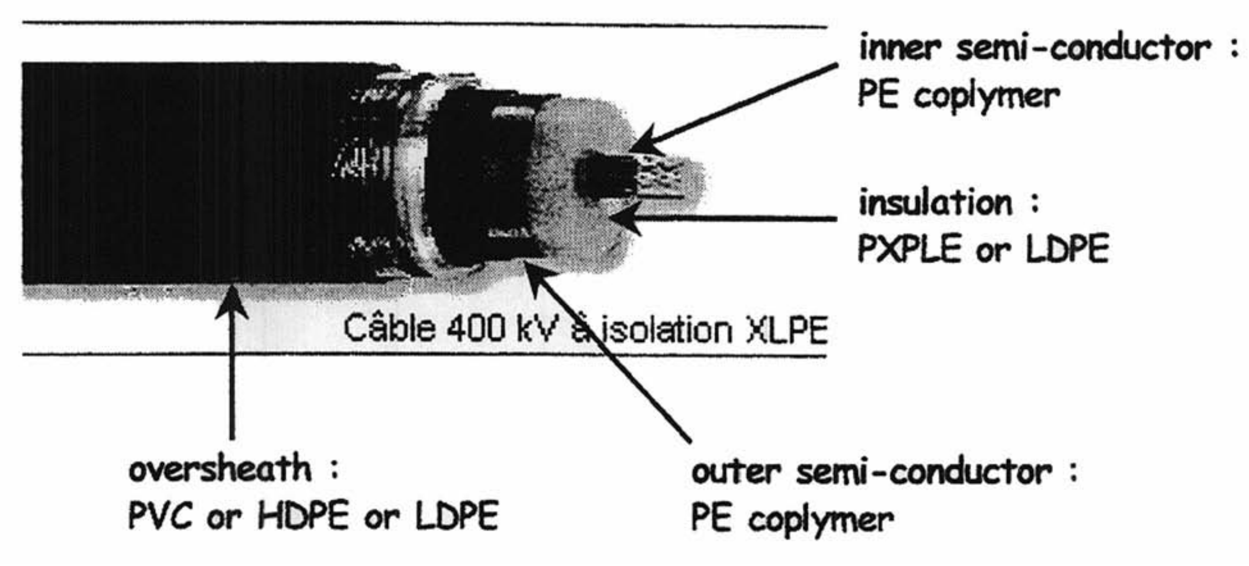

Figure 3-1
Description of 400 kV Cable with XLPE Insulation

3.2 Accessories

Among cable accessories, we cite only those exerting a notable influence over the system, mainly connections and terminations (shown in Figure 3-2).

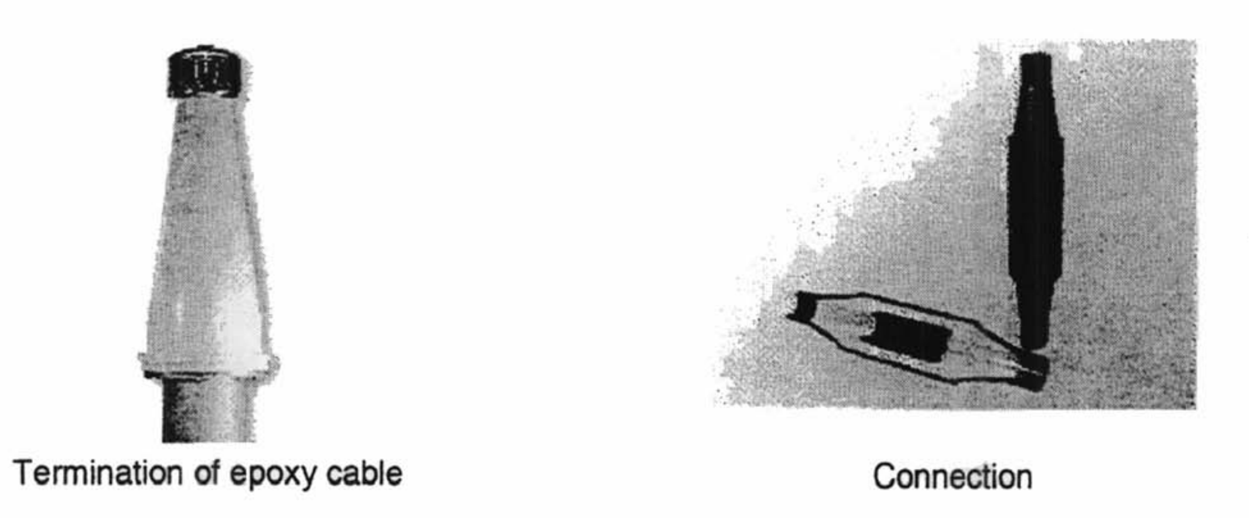

Figure 3-2
Description of Accessories

The operating principles are described in detail in the ADELAIDE guide to underground transmission lines [1]. There are several concepts for terminations and connections:

- molding using a pre-molded block
- taping, using synthetic insulating tapes

In all techniques, the critical points are at the outer semi-conductive shield cut-off (zone of intense electrical field gradient). With molded techniques, reconstituting the internal semiconductor is also a delicate operation, due to the heat constraints for injected insulation material.

3.3 Specifications

Material design must meet the standards used to qualify it, which are HN 33-S-53 and HN 33-S-52, respectively for EHV and HTB cables, and HN 68 S-23 for accessories.

These specifications detail tests required to verify functional withstand. Take, for example, the specification of synthetically insulated single core cables designed to operate at nominal voltages in the range of 225 kV to 400 kV.

Description of HN 33-S-53 (Now 33C 253)

The tests required by the standard relate both to the components taken separately and to the complete cable. They also take into account the cable and accessories that make up the full line. We shall detail only tests relating to organic materials.

- Insulation: chemical characteristics (initial and after aging), physical characterization (density of cross-linking measured by an elongation test under raised temperature, and melting point).
- Semi-conductive shields (over core and insulation): electrical resistivity.
- Jacket (oversheath): mechanical characteristics (initial and after aging) thermal stability (by measurement of loss of mass, measurement of pressure withstand under heat, measurement of mechanical properties when cold, measurements of withstand to cracks), physical characterization (density of cross-linking).
- Complete cable:
  - non-electrical tests: compatibility of components, evolution of mechanical properties after aging and under raised temperature, shrinking test, checks on water-tightness, test of flame non-propagation
  - electrical test: long and short duration (6000 hours) on complete cable and on cable and accessories

4
DESCRIPTION OF MATERIALS

Table 4-1 shows the component materials identified in the cables and accessories studied, from available manufacturer data. The table shows that the data on the materials supplied by the manufacturer are limited to the family of the base polymer. This list is not exhaustive but has the merit of highlighting the small number of base polymers used in HTB cables and accessories (basically PE, EPDM and Silicone).

Table 4-1
Nature of Basic Materials in Products under Study

Material	Component	Materials	Family
Cable	Insulating material	HDPE, LDPE	Thermoplastic
		Cross-linked PE (XLPE)	Thermosetting
	Jacket	HDPE, LDPE, PE	Thermoplastic
		PVC	
		Cross-linked PE	Thermosetting
	Semi-conductive shield	*No indication*	-
HTB connection	Electrical field redistribution insulator	EPDM	Elastomer
	Insulating material	Silicone	
	Jacket	EPDM	
HV high voltage		Silicone	Elastomer
		EPDM	
	In qualification	Epoxy/glass covered by silicone	Thermosetting

PE: Polyethylene – HDPE, LDPE: high, low density PE
EPDM: terpolymer Ethylene Propylene Diene rubber of ASTM D1418 type M

On the other hand, the composition of synthetic materials making up the cable and its accessories may be very complex. The base polymer is mixed with a number of additives and fillers, whose role is to change the physical and chemical properties of the material. The art of the formulator resides in the mixing of sufficient quantity of fillers and additives into the base polymer, so that the material properties meet specifications.

4.1 Base Polymer

Polymeric materials can be divided into 3 categories: thermoplastics, elastomers, and thermosetting materials.

- Thermoplastic polymers: have the property of reverting to their initial state after successive heating and cooling. These are the polymers most frequently used.
- Elastomers: distinguished from thermoplastics by difference in behavior in terms of rigidity, deformability, and resilience. Their characteristic is vitreous transition at a temperature lower than ambient (rubber state at T_{amb}).
- Thermosetting materials: constituted by three-dimensional macromolecule, can not be reversibly modified under heat.

These different families of polymers are distinguished by their viscoelastic behavior.
When subjected to mechanical deformation at a certain frequency, their mechanical response (dynamic spectrum shown in Figure 4-1) will depend on their molecular structure.

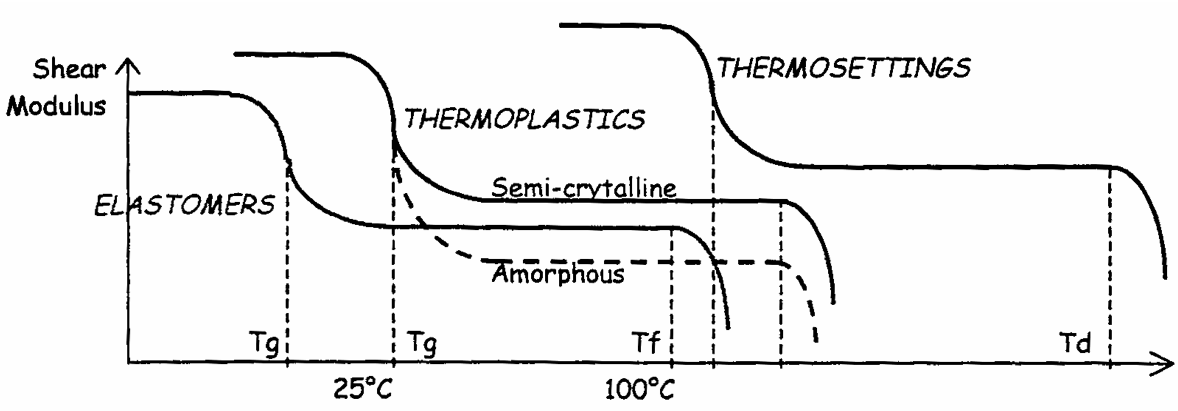

Figure 4-1
Thermo-Mechanical Behavior of the Three Families of Polymers

The basic polymers making up the materials of Table 4-1 are polyethylene (PE), EPDM and silicone.

Polyethylene is the basic polymer in many formulations and takes a number of forms [2]:

- thermoplastic (low or high density)
- thermosetting (by cross linking either by addition of peroxide or the use of silane)
- semi-conductive thermoplastic (by addition of a conductive filler)

PE suppliers are Borealis and Dow (formerly Union Carbide).

The parameters influencing PE are:

- the degree of branching or hanging chains which affect the crystallinity of the polymer
  - Low density PE: high degree of branching
  - High density PE: low degree of branching
- unsaturation rate: affects polymer stability

Cross-linked polyethylene appeared in the 1970s. Initially used in HTA cables, it is now used as an insulator in EHV cables, by means of sophisticated, leading edge technologies which not only improve the raw materials in use, but introduce manufacturing design improvements (e.g., triple-layer extrusion from a single device to give perfectly smooth and uncontaminated interfaces between the inner semi-conductive shield, insulation, and outer semi-conductive shield).

The cross-linking occurs by different methods:

- peroxide cross-linking
- silane cross-linking
- radiation cross-linking

EPDM is an elastomeric terpolymer constituted from ethylene, propylene, and diene monomers [3]. The three diene co-monomers commonly used and available on the market are:

- 1- 4 hexadiene
- dicyclopentadiene
- ethylidene - 5 norbornene

Silicone elastomers are classed into two categories depending on their mode of vulcanization [4]:

- Room-temperature vulcanization (RTV): cross-linking occurs by condensation reaction between the polymer and silane cross-linking material in the presence of tin dibutyl dilaurate, or in the presence of water with tin octoate as the cross-linking agent. Alternatively cross-linking occurs by addition of SiH-based cross-linking material at the double-bonded terminations of the polymer in the presence a lead catalyst, in a twin-compound process.
- High temperature vulcanization (HTV): cross-linking occurs essentially by peroxide initiation on copolymers with certain content of vinyl constituents, and in recent times by high-energy radiation. Sulfur is no longer used, due to the shortfall in the mechanical properties of the resulting vulcanized material. The vulcanization temperature depends on the nature of the peroxide employed.

The average molecular mass of the polysiloxane depends on the mode of vulcanization:

- between 400,000 and 1,000,000 for HTV silicones
- around 20,000 for RTV silicones

4.2 Fillers

A filler is any inert material (of mineral or plant origin) which when added to a base polymer causes substantial modification in mechanical or thermal properties, in such a way as to improve surface quality (in which case the filler is termed reinforcing) or reduce the cost of the material after transformation (termed non-reinforcing).

Fillers may be:

- natural organic
- synthetic organic
- mineral
- metallic
- metallic hydrates and oxides
- glass fillers
- carbon based fillers

The complete list is shown in Appendix A.

4.3 Additives

The term additive is used to describe materials which are physically dispersed in the polymer matrix without significantly affecting the molecular structure of the polymer. Adjuvants are compounds which when added in low doses have no influence on final properties, whereas additives are present in higher doses and may change the characteristics of the materials. The efficiency of an adjuvant is related to its dispersion and its compatibility with the polymer.

The major families of additives shown below are more precisely described in Appendix B.

- plasticizers
- stabilizers (anti-oxidants, anti-UV)
- lubricants
- colorings
- anti-impact agents
- anti-static agents
- flame retardants

The diversity of the additive materials is an indication of the complexity of the resulting materials. Each additive plays a specific role. If they are no longer present (by migration, exudation, or decomposition) the result can be drastic modification in the properties of the material and its ability to withstand its service conditions.

4.4 Structure Property Relations

When the structure of the material as a whole is known, it may be possible in some cases to work back to the general properties of the material, by establishing the structural/property relationships involved. Many studies have shown the links between the structural parameters of the polymer, the type and rate of fillers and additives, and resulting properties under various stresses, either they are physical, mechanical or electrical, dielectrical or withstand to age. The relationships that exist between the polymer structural parameters and properties are not always universal. This means that they depend on the nature of the basic polymer. The results which occur in a particular polymer may not be transferable to another. However, the structural parameters studied remain the same. On the basis of these observations, our initial objective was to determine the major structural parameters. At a second stage, a detailed bibliographical study on the structural/property relationships of various basic polymers will be necessary.

4.4.1 Basic Polymer

It should also be specified that, for a comprehensive structural study [5] the polymer must be studied in three different structural levels:

- molecular level: determination of the monomer motif
- macro-molecular level: arrangements of monomer motifs which form linear, ramified or three-dimensional polymers
- supra-molecular level: presence of amorphous or crystalline zones

At molecular level:

- Nature of monomer motif:
  - Ethylene: $CH_2{=}CH_2$ for Polyethylene $[CH_2–CH_2]_n$
  - Ethylene chloride $CHCl{=}CH_2$ for PVC $[CHCl–CH_2]_n$
  - Si-O-Si- for silicone
- Existence of irregularities: unsaturations, end of chains
- Tacticity

At the macro-molecular for linear polymers

- Homopolymer (arrangement of a single type of monomer) or copolymer (several types of monomer):
  - Ethylene and propylene to form the EPR copolymer
  - Ethylene, propylene and Diene Monomer to form the terpolymer EPDM
- Degree of polymerization n: related to average molecular mass by number (M_n), or average molecular mass by weight (M_w)
- Index of polydispersity IP: distribution of length of chains

- Existence of ramifications: result of secondary polymerization reactions

At the macro-molecular scale for three-dimensional polymers

- Homopolymer or copolymer
- Density of cross-linking: related to the average mass between nodes (M_c), node functionality (f)
- Cross-linking system: peroxide. sulfur, silane, radiation
- Chemical or physical bridging (interpenetration)

Super-molecular level:

- Crystalline or amorphous zones: crystallinity rate, size and morphology of crystallites
- Polymer mixtures: miscible or immiscible (phase separation)

4.4.2 Fillers

In addition to the chemical nature of the filler, the determining parameters are as follows:

Macroscopic level:

- content
- dispersion

Microscopic level:

- particle size rating
- morphology
- surface treatment

4.4.3 Additives

The analysis of additives involves the knowledge of:

- chemical family: determining the function, mode of operation (primary or secondary), the mode of deterioration and possible synergies
- additive content

5

CHARACTERIZATION TECHNIQUES

Table 6-1 shows the analytical techniques identifying the structural parameters required for the study of materials. Also indicated is whether or not a means of testing is available.

Some tests were recommended in the expert guide for power station cables [6] and are considered as easy to implement, among these being IRSP and TGA.

However, even for simple tests, results cannot always be directly interpreted. The results often defy direct interpretation. The qualitative analysis of additives is highly complex, and requires the use of an exhaustive database. The difficulty is increased due to additives being present in very small quantities in the mixture. The analysis of fillers when simple techniques are used does not give any indication of the surface treatment undergone by the fillers.

Once the determining structural parameters and the associated characterization techniques have been identified, we undertook the physical and chemical analysis of the various materials, in order to judge the degree of complexity of techniques used in the characterization and interpretation of data.

6
CASE STUDIES

The first case study involved 225 kV cable. Initial characterization of the insulation portion was used as a benchmark when finalizing techniques for laboratory characterization.

In order to assess the difficulties of analyzing an unknown material, we selected several HTB materials, while ensuring that the nature of the material was not always known. The study of the termination and of an accessory was performed in the HTA field (samples available). We tried to select materials belonging to different families to cover a wide range of formulations. (See Table 6-2)

Table 6-1
Technical Characteristics of Materials

Polymers	Information	Techniques	Availability
molecular level	monomer motif(s)	IRSP	EDF
	irregularity (unsaturation, ramifications)	IRSP or MNR	
macro-molecular level	linear polymer: M_n, M_w and IP	SEC or viscosity	CTA
	three-dimensional polymer: M_c	swelling, DMA	EDF
supra-molecular level	vitreous transmission, fusion, rate of crystallinity, multiphase system	DEA, DMA	
Fillers	**Information**	**Techniques**	**Availability**
macro level	quantitative analysis	TGA	EDF
	qualitative analysis	GC/MS, IRSP, elementary analysis	CTA, LRCCP
micro level	Morphology, particle size rating, surface treatment	SEM, TEM	EDF
Additives	**Information**	**Techniques**	**Availability**
	water content	Karl Fisher	EDF
	quantitative analysis	solvent extraction	
	qualitative analysis	GC/MS, TLC, IRSP	CTA, LRCCP

IRSP: Infra-Red SpectroPhotometry
MNR: Nuclear Magnetic Resonance
SEC: Steric Exclusion Chromatography
DMA: Dynamic Mechanical Analysis
TGA: Thermo-Gravimetric Analysis
DEA: Differential Enthalpy Analysis
GC/MS: Gas Chromatography coupled to Mass Spectrometry
SEM: Scanning Electron Microscope
TEM: Transmission Electron Microscope
KF: Karl Fischer
TLC: Thin Layer Chromatography
CTA: *Centre Technique d'Arcueil*
LRCCP: *Laboratoire de Recherche sur les Caoutchoucs et les Plastiques* (Rubber and Plastics Research Laboratory)

Table 6-2
List of Materials Selected for Case Studies

N°	Material	Voltage Range	Component	Material	Family
C1	Manufacturer A cable	225 kV	Insulating component	cross-linked PE	thermoset
C2	Manufacturer A cable	225 kV	Oversheath	PE	thermoplastic
C3	Manufacturer A cable	225 kV	Semi-conductor	?	?
C4	Manufacturer B cable	225 kV	Insulating component	cross-linked PE	thermoset
C5	Manufacturer B cable	225 kV	Oversheath	PVC	thermoplastic
C6	Manufacturer B cable	225 kV	Semi-conductor	?	?
E1	Interior end	HTA	Outer protection	silicon	elastomer
J1	Pre-molded connection	HTB	Insulation	EPDM	elastomer
P1	Transition piece	HTA	Part C	?	?
P2	Transition piece	HTA	Part B	?	?

6.1 Analyses Performed

The applications and limits of techniques employed at EDF (MPE laboratory) and by the LRCCP (GC/MS) are shown in Table 6-3.

Table 6-3
List of Analyses in Test Cases

Method	Application	Limits
Beilstein Test	Presence of chlorine in the material	
Solvent swelling test	Rate of cross-linking in material	Requires a large number of samples
Differential Enthalpic Analysis	On few samples: temperature of vitreous transition, melting temperature, crystallinity, physical ageing, phase segregation, cross-linking exothermic reaction, oxidation withstand	Method relatively insensitive to vitreous transition temperature
Thermogravimetrical Analysis	On small quantities of samples: thermal stability, combustible and non-combustible fillers	Interpretation by comparison to benchmark samples (no database)
Infra-red Spectrophotometric (by ATR)	On massive sample or low filler films or powder: chemical structure of basic polymer, presence of impurities	Relatively non-discriminatory method, interpreted by comparison to Hümmel database
Infra-red Spectrophotometric by transmission (after pyrolysis)	On carbon black filled samples	Relatively non-discriminatory method, interpreted by comparison to Hümmel database
GC/MS	On liquid extract samples	Small quantity of additives by dilution in solvent
DMA	Temperature-related mechanical properties: thermal stability, vitreous transition, rubber elasticity	On standardized samples ($60*10*2$ mm^3)
Karl Fisher	Water content in samples	

6.2 Results

These analyses are covered in the detailed test report which forms part of Ingrid Sellier’s master’s degree [7]. Tests relating to additive analyses (solvent extraction and infra-red spectra and chromatograms of extracts), and tests relating to the study of cross-linking density (by extraction in xylene or swelling tests) were entrusted to LRCCP [8]. Supplementary tests on another manufactured cable were also performed to assess possible differences in formulation and to test uncertainty of measurement.

Information relating to the polymer is shown in Table 6-4, and relating to fillers and additives in Table 6-5. The interpretation of experimental results is commented by family of polymers: PE, EPDM and Silicone.

Table 6-4
Summary of Results on the Basic Polymer

N°	IRSP (method used)	DEA			Gel Rate (Xylene)	Swelling (Cyclohexane)
		T_{melt}	Crystallinity	$T_{annealing}$		
C1	PE*(ATR)*	111°C	27%	80°C	18%	x
C2	PE*(ATR)*	131°C	50%	no	x	x
C3	PE-EVAmixture (pyrolysis)	75°C-87°C	10%	no	26.5%	x
E1	Silicone *(ATR)*	-	-	no	x	210%
J1	EPDM	x	x	no	x	230%
P1	EPDM (pyrolysis)	-	-	no	x	x
P2	EPDM (ATR)	-	-	no	x	x

Table 6-5
Summary of Results of Analyses of Fillers & Additives

Nº	ATG		Extraction		GC/MS
	Organic Fillers (1)	Mineral Fillers (2)	In Acetone	In Mixture (3)	
C1	0	0	0.6%	2%	α-methylstyrene, acetophenone, cumylic alcohol
C2	0	0	0.3%	1%	series of hydrocarbons, BHT (anti-oxidant)
C3	38%	0	4%	16% (presence of white residue)	acetate diethyl, acetophenone, cumyl alcohol, phenol derivative
E1	0	30% under N_2 (SiO_2), 60% under O_2	4%	X	cumyl alcohol, siloxane derivatives
J1	0	35% (SiO_2)	7%	X	cumyl alcohol, DOA and DOP (adipate and phtalate plasticizers), phenolic derivatives
P1	40%	0	12%	X	X
P2	0	40% (SiO_2)	7%	X	X

X: tests not performed

(l) Percentage determined at decomposition temperature range of 450°C-700°C from test under nitrogen

(2) Residual percentage at 900°C

(3) Mixture: hexane/ethanol/chloroform in proportions of 4/1/1

6.3 Case of PE (C1, C2, C3)

6.3.1 Results on Polymer

Molecular level

- **Monomer motifs**: PE patterns for C1 and C2, and PE and vinylacrylate patterns for C3; the spectral difference between the pure PE and the material analyzed after pyrolysis highlights the presence of ester functions characteristic of the acrylate motif (COOR where R = CH_3 or CH_2CH_3) (around 1710 cm^{-1}). The spectra of the inner and outer screen are rigorously identical.
- **Ramification rate**: C1: 8/1000C.
- **Unsaturation rate**: not performed.

These parameters are accessible by various techniques: IRSP and MNR [9]. Only the IRSP analysis was performed in our study. The bands studied were as follows:

Ramification: 1378 cm^{-1}: CH_3 characteristic of rate of ramification

Unsaturation: 964 cm^{-1}: vinyl (trans); 910 and 990 cm^{-1}: vinyl; 888 cm^{-1}: vinylidene

BORÉALIS performed the quantification of the **unsaturation bands** on the polymer before cross-linking. Unsaturation bands were present in relatively small quantities (in the order of 0.2/1000 carbon).

Ramification rate was determined by MNR using BORÉALIS to indicate a proportion of loose chains (type C4 and higher) in the order of 13/1000 C for a polymer qualified as low density.

The different bands are still visible on the IR spectrum (transmission) after pyrolysis of the isolator (cross-linked) with significant intensities. The determination of the ramification rate on our spectrum (after cross-linking) indicates a rate of loose chains in the order of 8/1000 C (close to the results given by BORÉALIS). However, we could not assess the length of the loose chains using the IRSP method.

Macromolecular level

- **Average molecular mass**: the determination of this parameter for linear PE requires the use of a temperature-related steric exclusion chromatograph. This test was not performed.
- **Inter-node molecular mass**: this parameter is proportional to the rate of swelling in a solvent. The gel rate values allow comparisons to be made in terms of material cross-linking, but do not allow for quantity determination of the density of cross-linking. From this measurement, one can conclude that 18% by mass of C1 sample is cross-linked. In the C3 sample, interpretation is possible due to the presence of carbon black fillers that remain in the insoluble fraction.
- **Mode of cross-linking**: according to the manufacturer, the isolator C1 is chemically cross-linked using peroxide. The cross-linking agent is classically **dicumyl peroxide**, content 2%. It is known that the cross-linking agent is completely consumed in the reaction, but gives out

the following decomposition by-products: **acetophenone, α-methylstyrene and cumyl alcohol**. It is therefore impossible to determine the exact nature of the cross-linking agent. However, we were successfully able to identify the presence of the decomposition products by GC/MS (in C1 and C3, which indicates that C3 sample was cross-linked using dicumyl peroxide). Cumyl alcohol was also evidenced by means of infra-red analysis (characteristic bands at 3386, 1278, 1072, 953, 859, 763, 699 cm^{-1}).

Supra-molecular level

- **Vitreous transition temperature** (Tg): less than 25°C.
- **Melt temperature** (Tf) and **crystallinity rate**: Thermal analysis differentiates between low density PE and high density PE, in as much as the ramification rate influences the melt temperature and rate of crystallinity (Table 6-6). Cross-linking also affects changes in morphology. Caillot has shown that melt temperature and crystallinity reduce with the rate of cross-linking [10].

Table 6-6
Morphological Analysis of PE by AED

	LDPE	HDPE	XLPE
Melt start (°C)	50	80	50
T melt (°C)	105-115	125-135	100-135
Crystallinty (%)	43-50	55-65	35-40
Case studies		C2	C1

- **Annealing temperature**: Thermo analysis (AED) gives insight into the thermal history of the material, due to there being a secondary endothermic peak characteristic of the reorganization of the crystallites after annealing [11]. Hence sample C1 was annealed at a temperature of 80ºC (post-heating temperature to complete cross-linking).
- **Multi-phase system**: Sample C3 of the semi-conductor is a mixture of polymers which are within themselves not miscible insofar as there are two melt peaks, one at 75ºC, and the other at 87 º C.

A bibliographical study of EVA ethylene-vinyl acetate copolymers (VA: CH_2=CH-$COOCH_3$) has shown that for a rate of VA less than 40%, the copolymer is crystalline. The melt temperature of the copolymer reduces as the VA co-monomer relative content increases. The results of a number of investigations on this question are summarized in Table 6-7.

Table 6-7
Influence of the VA Relative Content on the Crystallinity of an EVA Copolymer

Reference	VA Relative Content (%)	Melt Temperature (°C)	Crystallinity (%)
[12]	16.5	90	
[12]	22	82	
[13]	5	105	34
[13]	10	95	28
[13]	14	82	24
[13]	17	79	21

In the case of a 75% EVA mixture (22% VA) + 25% LDPE, the AED spectrum shows two melt peaks, corresponding to the melt peaks for EVA copolymer and LDPE, respectively.

On the other hand, the thermo-gravimetrical analysis (ATG) under oxygen shows the two stage deterioration occurring at 316°C and 470°C, respectively. It has been shown that the loss of mass, observable at 360ºC in the case of a EVA/XLPE mixture, tended to increase when EVA relative content was higher, and that a second loss of mass was observable at 460°C [14].

It may be concluded that the **basic polymer for semi-conductor screens** is a **mixture of peroxide cross-linked polyethylene** at a low melt temperature (87°C) and an **ethylene-vinyl acetate copolymer**, characterized by a relatively substantial content of the VA motif (melt temperature 75°C). Although the infra-red spectrums of the inner and outer screens appear to be identical, the AED and TGA thermograms are slightly different. This shows that the polymer content in the mixture is different as also the relative content of vinyl acetate in the EVA copolymer.

6.3.2 Results on Fillers and Additives

- **Fillers-**: It is interesting to note that samples C1 and C2 are totally exempt of filler. The materials for very high voltage applications are extremely pure. For the C3 semi-conductor screen, the filler in carbon black attains 38% by weight. This high value is required to ensure optimal electrical conductivity.
- **Additives**: The composition of cross-linking and anti-oxidant agents is known for the XLPE insulating (C1). The **anti-oxidant** is Santonox (4,4'-thiobis(2-(1,1-dimethylethyl)-5-methylphenol). Identification is possible after extraction of powdered XLPE in methanol at room temperature followed by qualitative analysis by HLPC [15].

However, it has been shown that in a fully cross-linked sample, it is impossible to detect the anti-oxidant, because the additive sticks to the polymer chain in the cross-linking process and is no longer extractable by methanol.

The quantity of product extracted in samples C1 and C2 is very low (< 2%), and is slightly greater for C3 (4% in acetone). For the C3 extract, in addition to the peroxide decomposition products, a phenol derivative (probably an anti-oxidant), has been detected.

As regards C3, 16% of extract can be obtained with a more appropriate solvent mixture. This is not a clear extract but a white residue. The spectral comparison in infra-red, as compared to the classic database, gives reason to believe that this is an EVA fraction which may have crystallized in this solvent mixture.

6.4 Case of EPDM (J1, P1, P2)

6.4.1 Results on Polymer

Molecular level:

- **Monomer motifs**: The IR spectrum absorption bands can be attributed for an EPDM resin [16]. This provides an indication of copolymer composition on the basis of a study of intensities at 1150c1/720cm^{-1}. In the P1 spectrum (after pyrolysis), substantial bands at 1380 cm^{-1} (vibration of C_ H in CH_3), at 1460 cm^{-1} (vibration of C_ H in CH_2), very small bands at 1150 cm^{-1} (vibration of an isolated methyl grouping), and at 720 cm^{-1} (long chains of CH_2 units with n>5, whereas the shorter chains $(CH_2)_3$ and $(CH_2)_2$ absorb at 732 cm^{-1} and 751 cm^{-1} respectively). The equation when applied to P1 gives a propylene/ethylene proportion of 1/6. For P2, band intensity at 1150 cm^{-1} is too weak to be analyzed. For J1, the silicon filler prevents any interpretation in this zone. According to this approach, the content in diene motifs is considered to be very low. However, the nature of the diene comonomer remains elusive.
- **Irregularities**: impossible to analysis in the mixture.

Macro-molecular level:

- **Critical mass between nodes**: swelling rate (on J1) provides access to Mc by Flory-Rehner equation calculation [16]. The calculation in our case gives a critical mass value between nodes of 1200 g.mol^{-1}.
- **Cross-linking system**: the cross-linking of the EPDM may take place in a number of ways [3]: sulfur vulcanization: disulfur bridge peroxide vulcanization.

Samples tested appeared to be peroxide cross-linked, as we were unable to detect bands attributable to disulfur bridges.

6.4.2 Results on Fillers and Additives

- **Fillers**: The J1 and P2 samples were **filled with silica type minerals**. Silica type mineral fillers subjected to quantitative analysis under inert atmosphere gave content at 35% and 40%, respectively. The analysis under oxygen revealed decomposition of fillers at temperatures above 340°C without changing residual content. The fillers were identified by IRSP analysis after ATG. The P1 sample was filled with carbon black. For quantitative analysis of the **carbon black**, passing under O_2 atmosphere is recommended at temperatures of 600°C [17].
- **Additives**: The analysis by IRSP of additives, although present in substantial quantities (up to 12%), is not conclusive. The bands resulting from low molecular mass polyethylene mask the presence (if any) of other compounds. On the other hand, chromatographic separation followed by mass spectrometry analysis evidences cumyl alcohol (a decomposition product of peroxide) as well as plasticizers (dioctyl phthalate and octyl adipate), as well as high molecular weight compound, a phenol derivative which could be an anti-oxidant.

6.5 Case of Silicon (E1)

6.5.1 Results on Polymers

- **Monomer motif**: IRSP spectrum in sample E1 is for a polysiloxane. There are, however, several materials in this family, as a function of the monomers used. The presence of vinyl motifs cannot be evidenced by IRSP. Vinyl co-monomers are often present in relatively small proportions and are used to improve cross-linking. Phenyl motifs are evidenced by the presence of bands at 1430 cm^{-1}, 745 cm^{-1} and 715 cm^{-1}. These bands are not clearly visible in the spectrum. We can therefore conclude that the spectrum of samples is very close to that of **PDMS (polydimethylsiloxane).**
- **Cross-linking system**: The presence of cumyl alcohol in the extract gives reason to believe that reticulation is by peroxide.

6.5.2 Results of Fillers and Additives

- **Fillers**: The thermogravimetric analysis of sample E1under an inert atmosphere gives residual content in **mineral fillers (silicon based)** of 30%, although the result is 60% under an oxidized atmosphere. This particular behavior is the result of the silicon elastomer resin decomposition reaction in an oxidized environment, leading to the formation of inert products (SiO_2) [18]. Hence the difference between residual content (30%) is the result of the silica degraded PDMS fraction. This silica decomposition is catalyzed by an oxide. The detailed analysis seems to show that this is silica with OH functions and hydrogen bonds (wide bands at 3400 cm^{-1}) to the polysiloxane chain.
- **Additives**: Only 3% of the extracts were collected. Infra-red analysis shows that this is a siloxane derivative. GC/MS identified peaks indicating cumyl alcohol (peroxide initiation), siloxane derivatives (of different molecular masses), and plasticizers (phthalates and adipates).

6.6 Discussion

The presentation of the results for three families of polymers analyzed, namely PE, EPDM and silicone, permits a number of conclusions:

6.6.1 Base Polymer

- Prior knowledge of the nature of the basic polymer is not necessary for a **homopolymer**. The spectrophotometric analysis rapidly identifies the polymer using a spectrum database (Hümmel database containing 30,000 polymer spectra).
- For linear PEs, determining the molecular mass requires steric exclusion chromotography measurements at raised temperature (not available at LRCCP).
- Once the base polymer is identified, an extremely detailed bibliographical study is required in order to identify all methods of determination of the structural parameter relating to the polymer in question. We have good knowledge in this field in the PE insulation and EPDM. The same does not apply to PE/EVA semi-conductor mixture, and to silicone. The spectrophotometric methods (transmission analysis) are often very useful.
- The spectrometric analysis is very difficult to interpret a **mixture**. Thermal analysis enables detection of the presence of non-miscible polymers (several melt peaks). In this case it is important to have a discussion with the formulator, if the respective content of the various polymers is to be determined.
- Quantitative analysis of the relationship of motifs in **copolymer** is difficult. It was possible in the case of EPDM copolymers only, by means of spectrophotometric analysis.

6.6.2 Fillers

- For analysis of fillers, thermal analysis is suitable for distinguishing organic and mineral fillers. It is however necessary to know the thermal decomposition reaction of the fillers in order to determine the absolute content.
- The distinction between the various mineral fillers would require additional elementary analysis. IRSP analysis permits the analysis of silicon only (with OH functions or otherwise). Similarly, morphological analysis (by TEM for carbon black or SEM for mineral fillers), provides access to more information (granulometry, dispersion…)

6.6.3 Additives

- Acetone is a good solvent for certain polymers (in particular EPDM and silicon), but is not suitable for all of them. Methanol extraction was used for PE additives [8]. A solvent mixture was also used, [8].
- The use of GC/MS for qualitative analysis of additives gives positive results when infra-red is used and when spectrum interpretation is inhibited by the extraction of low molecular mass PE chains, for example, C1, C2, C3, P1 and P2.

7

ORGANIZATION CHART

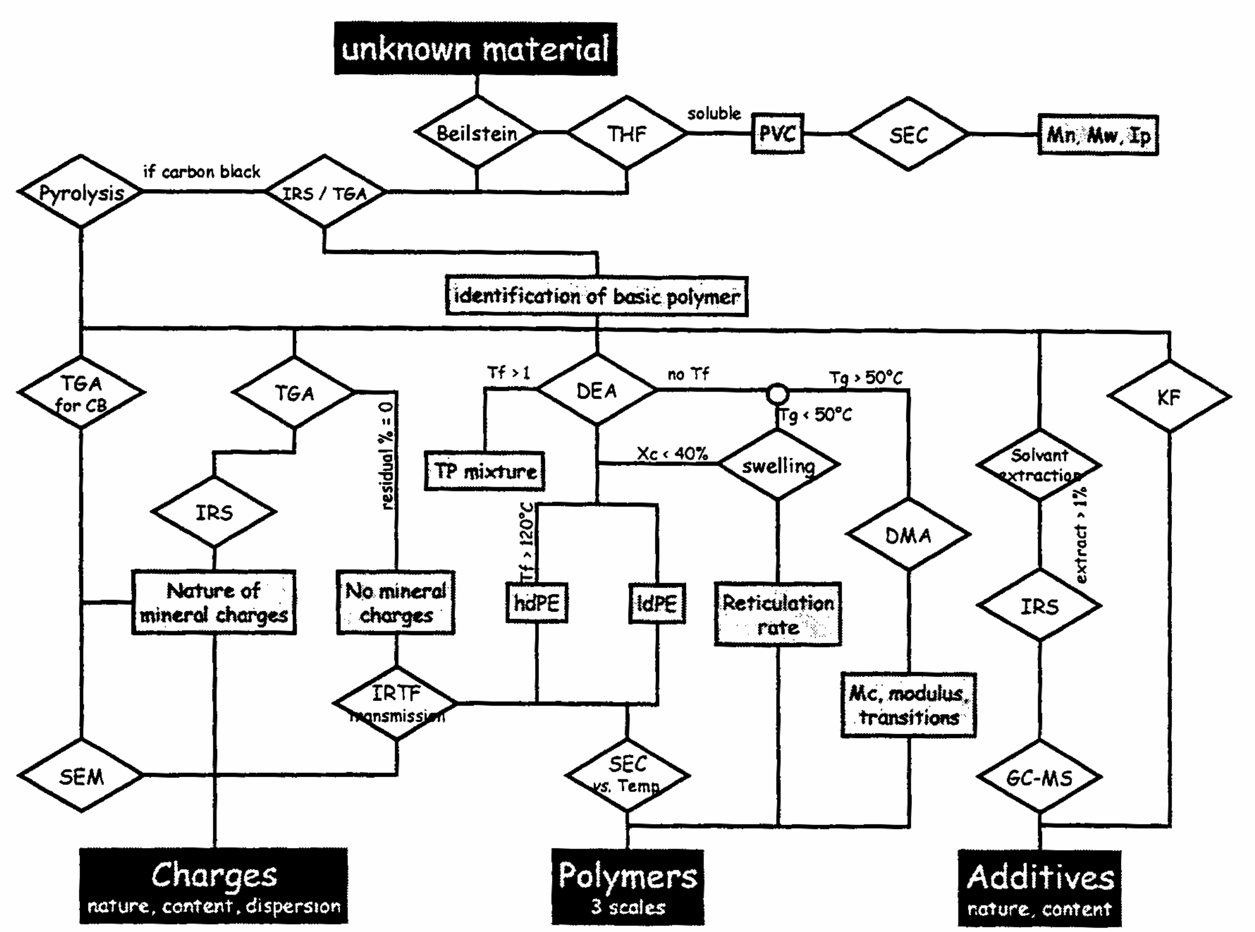

Figure 7-1
Organizational Diagram for Material Identification

8

CABLE AND ACCESSORY MANUFACTURERS

Discussions with cable and accessory manufacturers gave an understanding of their approach to materials. This involved either mixture at the production site or buying the mixture from a supplier, the introduction of the different constituents on one or more different production sites, and the mode of indication of modification to materials. Table 8-1 also shows the position expressed by persons met when implementing the Materials Identity Card approach (indicating priorities as the case may be).

Table 8-1
Discussions with Manufacturers

	Manufacturer A	**Manufacturer B**	**Manufacturer C**
Mixture on site	no mixing (working on various sites	PRC (insulator), semi-conductor, EPR (accessory: Italy)	PVC (oversheath), semi-conductor, EPR, silicone (working on a single site)
Supplier mixture	insulator, semi-conductor, sheath, accessories	PVC, PE (oversheath)	PRC (insulator), PE (oversheath)
In case of modification	**does not give notice**	no modification for 3 years	all modification indicated
Expectations	against descriptive approach possible for protection system	In // to functional approach interested by S/P relationships **priority** 1: oversheath **priority** 2: insulator	costly tests : long duration and climatic introduction time too long **priority** 1: accessories
Inhibitions	study already performed for isolation difficult to extrapolate to production	difficult for electrical properties impossible for accessories	**No**

These results give rise to a number of comments on the analysis of the basic polymer, additives, on the possibility of establishing structural property relationships, and on identifying functional withstand for the completed cable.

8.1 Insulation

A characteristic of the insulation is its purity, namely, the extremely limited number of additives entering into the formulation. It is necessary to have the mixtures filtered prior to extrusion. It is therefore relatively easy to achieve the desired material composition. However, the cable manufacturing process gives rise to a degree of material heterogeneity along the length of the cable. Observation of two crossed polarizers revealed that in certain manufacturing conditions and close to an inner semi-conductor, two crescent shaped zones have a more bi-refringent nature than elsewhere along the cable [19]. Birefringence, which is visible on Figure 8-1, has been attributed to the presence of residual stresses created at the time of manufacturing and fixed in the cross-linking. Their characteristic is a greater quantity of carbonyl links, a lower melting temperature and lower rate of crystallinity, a lower density and less anti-oxidant activity. All these structural parameters are indicative of an increase in cross-linking density.

Studies have shown that possible variances arising from aging are in fact considerably less than the discrepancies observable between zones of low and high birefringence.

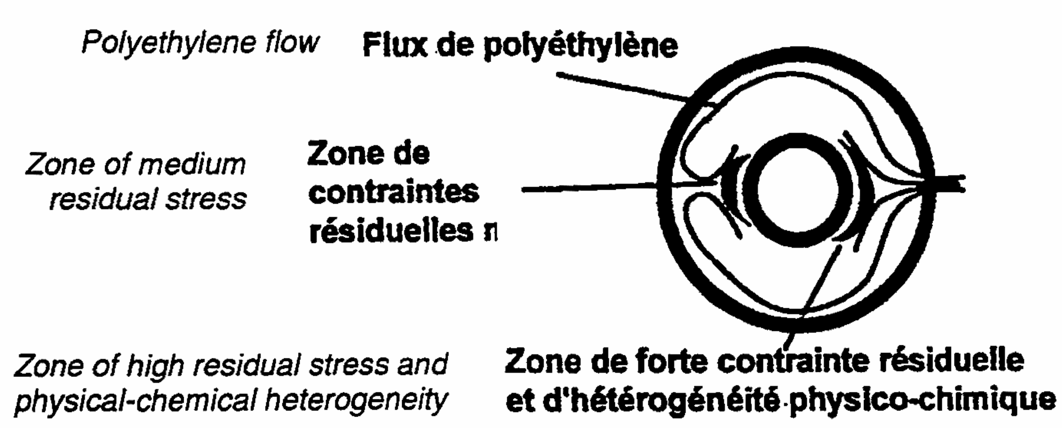

Figure 8-1
Zones of High Birefringence in the Cable and Material Flows

It is generally acknowledged that the reticulation density strongly influences mechanical properties. However, the divergences encountered in this study remain within the acceptable limits of specifications. This heterogeneity therefore does not play a major role in regards to material functionality. It may on the other hand indicate a long-term operating point of fragility.

Studies on the relationship of the PE structure (average molecular mass, rate of crystallinity, crystal morphology) and electrical properties (space charges, dielectrical rigidity) have been undertaken by Manufacturer A in collaboration with CEA. They showed that not only does crystallinity and molecular mass play a role in regard to space charges, but also to morphology (change induced by crystallization pressure) [20]. This result confirms the complexity of electrical-structural property relationships. These properties do not reflect atomic processes (active chemical space charges), but they are also strongly dependent on the fraction of free volume in the material, which acts as a space charge (chemically inactive).

8.2 Oversheath

This part of the cable does not play an electrical insulating function. It is therefore considered less critical. For this reason, Manufacturers A and B do not formulate their mixture. Manufacturer C, on the other hand, mixes its own PVC. Manufacturer B emphasized their complete dependence on suppliers of materials for mixtures used in the oversheath and therefore had concerns that any future modifications would affect the outer protection system.

The oversheath plays a role of external protection, particularly against humidity. The oversheath requires good mechanical properties at ambient, cold and hot conditions, and in the event of thermal shock. These properties must be sustained over time irrespective of temperature factors. Radial leak-tightness is also assured by the screen (lead and aluminum) which also diverts short-circuit currents. Manufacturer A therefore suggested adopting a system rationale, rather than considering separate materials. They preferred to speak about an **outer protection system** made up by the oversheath and screen.

8.3 Semi-Conductors

The specification HN-33-S-53 emphasizes the importance of this component, whose function is to homogenize the electrical potential. It is a fundamental requirement that the extruded layer be in good contact with the insulation. Many electrical magnitudes (resistivity, among others) depend on the quality of the semi-conductor screen (good adhesion of the insulation, absence of roughness, compatibility of the insulating material, no product migration). Semi-conduction properties are attained by incorporating carbon black fillers into PE or PVA copolymer, above a certain threshold (filler percolation threshold). Studies have demonstrated that semi-conductor product migration into the insulating material was observable under certain conditions, mainly acrylate functions penetrating the insulating material to depths of some few hundred microns. On the other hand, for a cable submerged in water at 70°C for 425 days, concentrations of water at 4,000 ppm were found in the semi-conductor (as against 1,000 ppm in a new sample, and 10 ppm for new LDPE) [21]. This shows that in conditions of water penetration, the semi-conductor may become a reserve of water which can, under the effect of temperature and the electrical field, diffuse into the insulating material at a later date.

The quality of the material used in this screen appears to be of the highest importance, especially due to the complexity of its composition. As with the oversheath system, Manufacturer A proposes using the term **insulation system** to take into account both the insulation and the inner and out semi-conductors.

8.4 Accessories

The accessories (2 terminations and 1 or 2 connections) form part of the short and long term electrical tests required to qualify the complete cable. Experience shows that they are often the weak point in the line and can be damaged by electrical breakdown. The manufacturers unanimously adopted a systems approach, to include cables and accessories. The composition of these accessories is highly complex. Manufacturers such as B and C used terms such as ‘formulations’ in which 20 or more may be used. Complexity arises from the elastomer technology implemented, which requires a very large number of additives; sometimes in very small quantities (we have an exhaustive list [22]). Tests showed that identification of these additives after mixing and cross-linking was extremely difficult, if not impossible.

Furthermore, the technology used, involving large items formed by the injection of considerable volumes of material, leads to heterogeneity in the final product. Analysis of the material in a limited area does not represent the volume as a whole. When establishing structural/property relationships, unsatisfactory results are present, insofar as they do not take into account the influence of actual faults, although they are of major importance in regard to the electrical properties of the accessories. However, it appears of great importance to track the way these materials are formulated, as any modification in the additives used can have significant consequences on electrical properties.

9

CONCLUSION

The Materials Identity Card approach proposed in these studies called under certain circumstances limit the number of functional tests required if qualification were to be extended after a change in materials. An approach is based on two principles:

- identification of material structural parameters (responsibility of the manufacturers and raw materials suppliers), as a basis for the institution of the Materials identity Card
- establishing structural/property relationships for the materials

From the present study, conclusions can be made in regard to the first of the two points. Structural parameters, accessible by means of existing characterization techniques and which can influence the properties of the material, have been identified. In practice, the analysis of the materials after formulation (after study of actual circumstances) is not always easy, as interpretation is somewhat hazardous, due to the presence of fillers. This difficulty highlights the need to collaborate with the manufacturers and suppliers of raw materials to access all the structural parameters. Furthermore, we were able to show that **morphology** is a key parameter influencing electrical properties, which results in the need to determine the fraction of free volume in the material. These aspects require further study.

Nevertheless, a general method of identification of materials has been developed, and is presented in the form of an organization chart of which important structural information can be accessed.

Finally, discussions with the manufacturers enabled us to closely identify not only requirements, but the actual circumstances in which this approach might be effective.

10
PERSPECTIVES

The interest of developing a Materials Identity Card approach lies in the structural / property relationships which must be established, if a decision is to be considered on the basis of the functional withstand of the material. This part of the second phase was completed. We therefore gave thought to the ways in which the relationship between structural parameters and material properties could be established (intrinsic physical properties and properties specified in the specification documents). We began with the observation that a quantum of information was already available from the manufacturers, and that such an approach was part of their core business (improving formulations in the light of properties required). The idea of setting up a database was raised. The database would have no interest unless it was dynamic and enabled conclusions to be drawn in regard to the influence on material properties of modifications in structural parameters.

After studying the possibilities of the **Quantitative Structure Property Relationship** (QSPR) **mathematical tool**, it appeared of interest to compile manufacturer data into it, and therefore generate mathematical relationships between the descriptors and the properties. Actual case studies, based on manufacturers' proposals, would enable the tool to be validated in practice.

The last stage in the approach involves working back to the level of the material itself. This difficult stage requires a clear vision of the material and functional tests. It could well be part of the aim of the project, proposed by J.C. Vérité, in regard to using modeling to reduce the cost and the lead time for qualification of transmission equipment. The study of how opportune it might be to go on with this project highlights the lack of relevance of modeling to the study of climatic and mechanical testing on the synthetically insulated cables. The Material Identity Card approach could make good on the shortfall in the event that an extensive qualification were required. On the other hand, the physical properties contained in the database could be used as input data for the various models.

11
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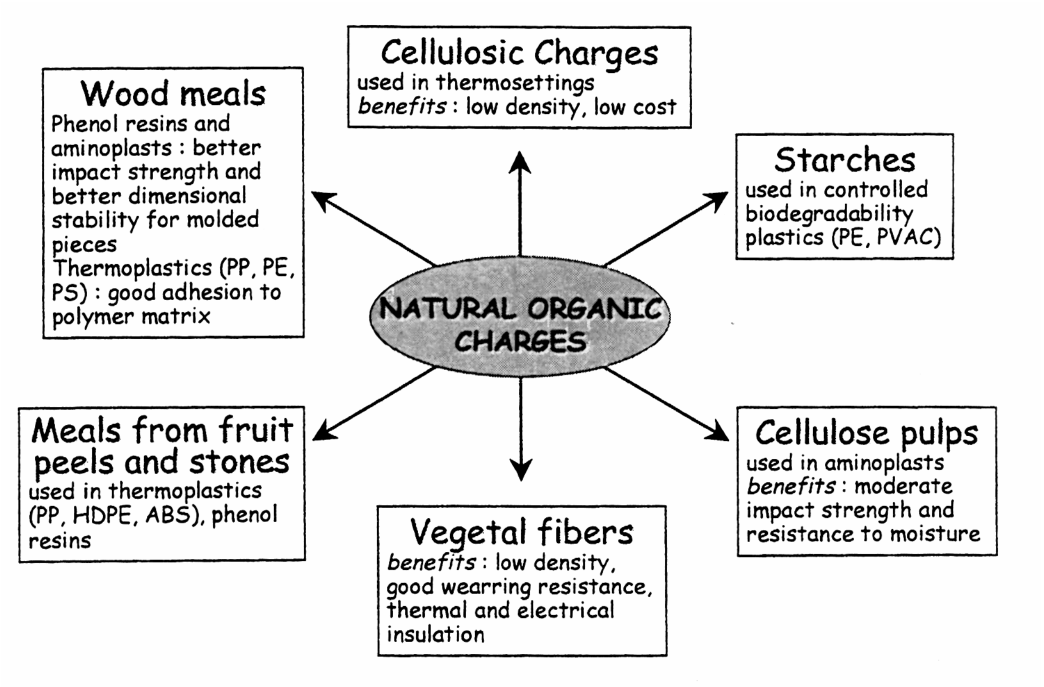
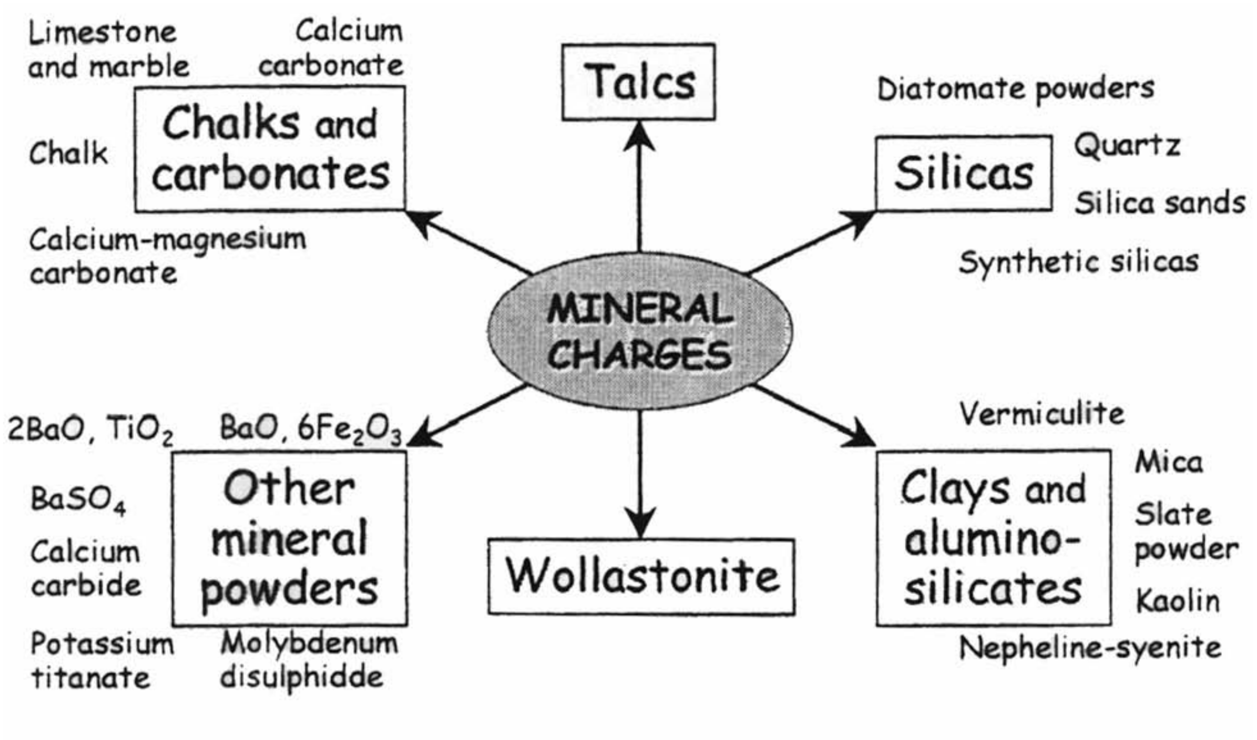
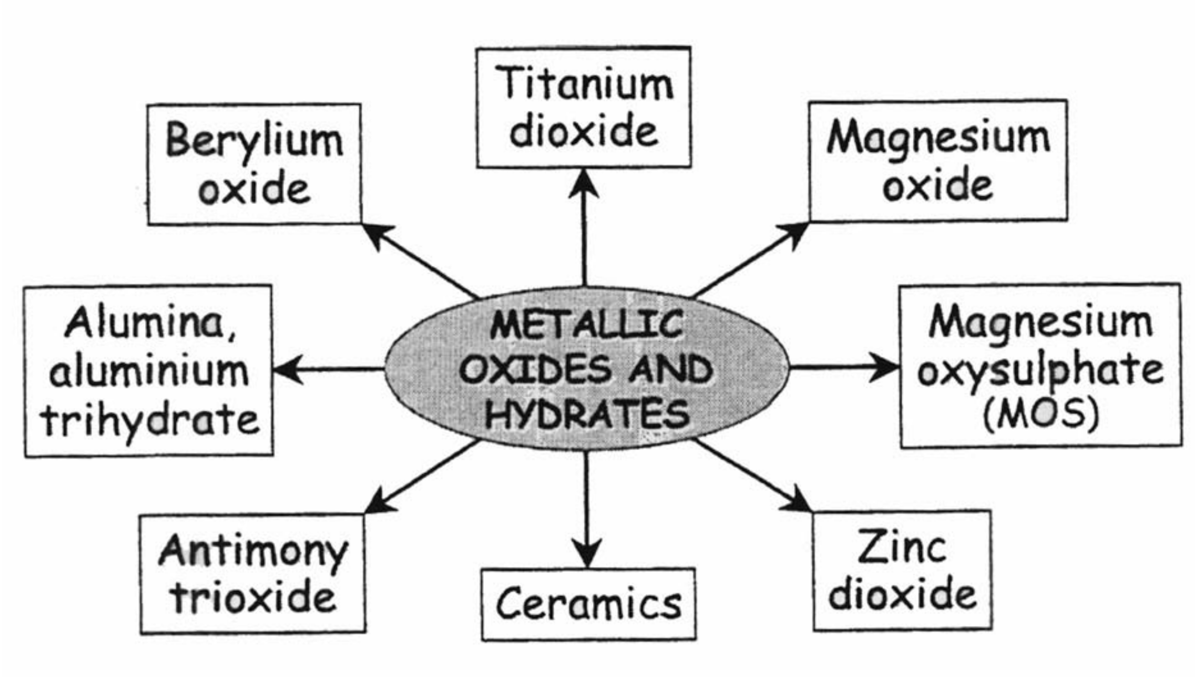
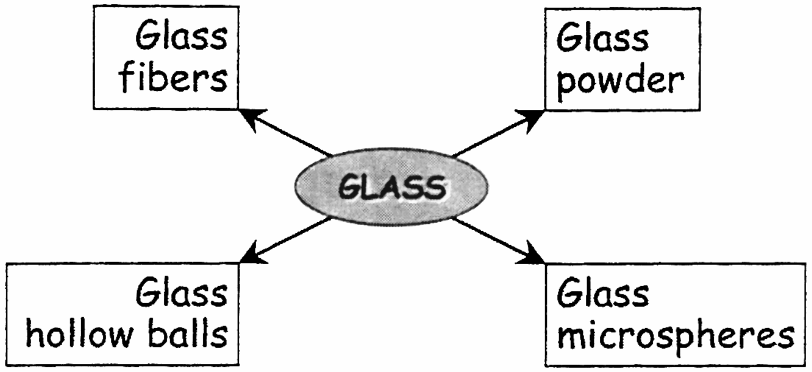
A
FILLERS

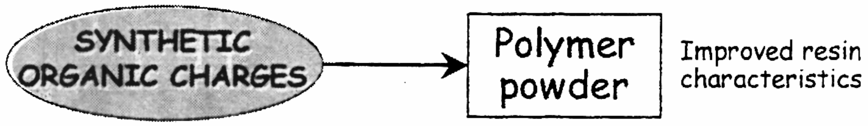
- Natural Organic Fillers
- Synthetic Organic Fillers
- Mineral Fillers
- Metallic Oxides and Hydrates
- Glass
- Carbon
- Metallic Fillers

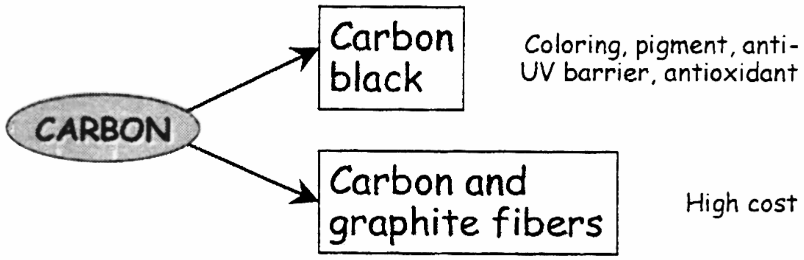


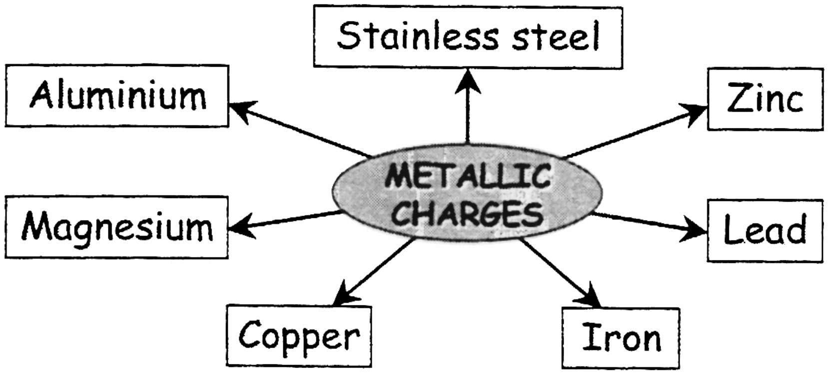

Limestone and marble
Calcium carbonate
Chalks and carbonates
Chalk
Calcium-magnesium carbonate
Talcs
Diatomate powders
Silicas
Quartz
Silica sands
Synthetic silicas
MINERAL CHARGES
$2BaO, TiO_2$
$BaO, 6Fe_2O_3$
$BaSO_4$
Other mineral powders
Calcium carbide
Potassium titanate
Molybdenum disulphidde
Wollastonite
Vermiculite
Clays and alumino-silicates
Mica
Slate powder
Kaolin
Nepheline-syenite


Berylium oxide
Titanium dioxide
Magnesium oxide
Alumina, aluminium trihydrate
METALLIC OXIDES AND HYDRATES
Magnesium oxysulphate (MOS)
Antimony trioxide
Ceramics
Zinc dioxide


Glass fibers
Glass powder
GLASS
Glass hollow balls
Glass microspheres


SYNTHETIC ORGANIC CHARGES
Polymer powder
Improved resin characteristics


Carbon black
Coloring, pigment, anti-UV barrier, antioxidant
CARBON
Carbon and graphite fibers
High cost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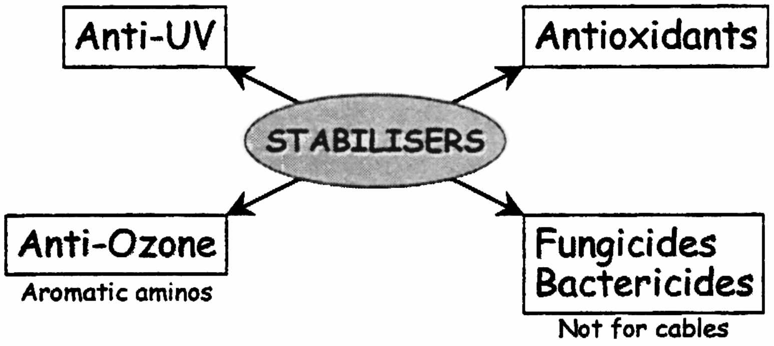
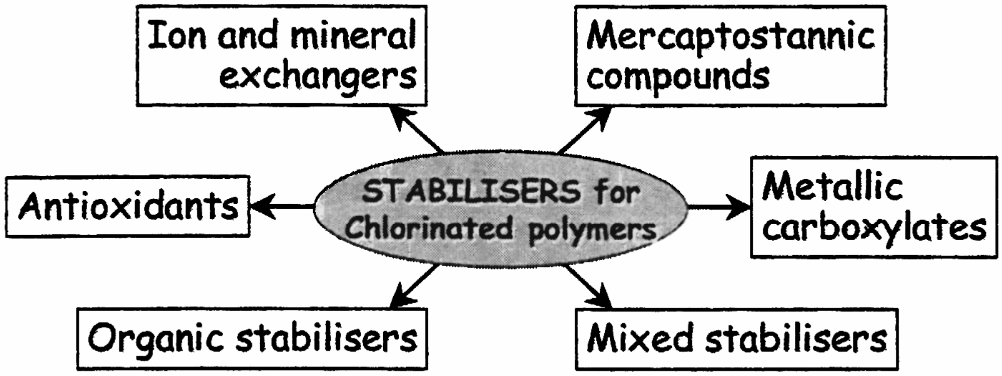
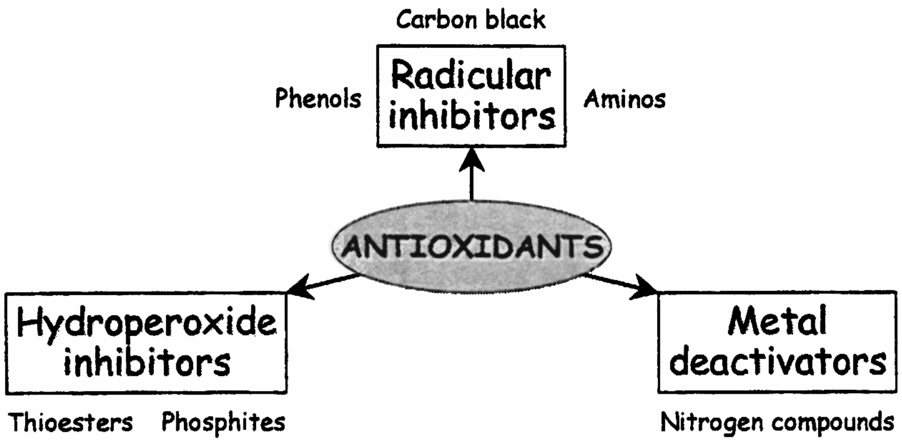
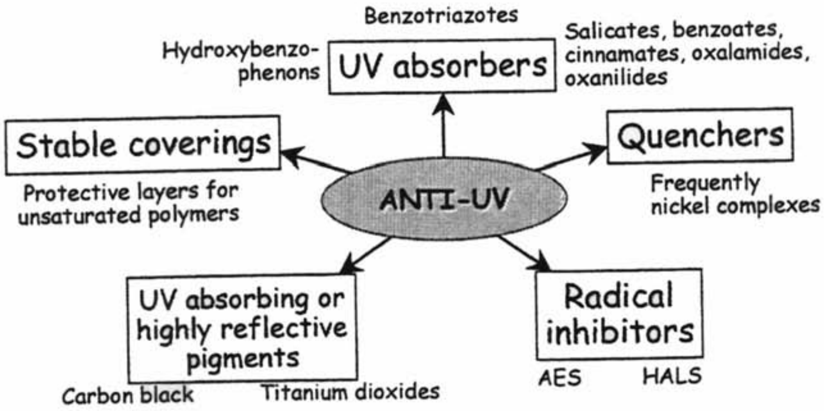
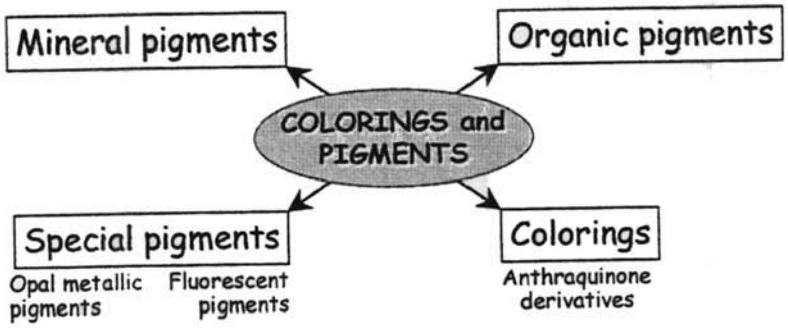
Aluminium
Zinc
METALLIC CHARGES
Magnesium
Lead
Copper
Iron

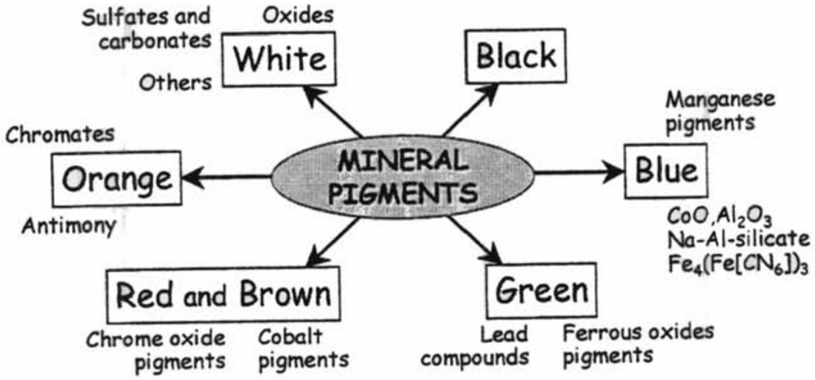

STABILISERS
Anti-UV
Antioxidants
Anti-Ozone
Aromatic aminos
Fungicides Bactericides
Not for cables

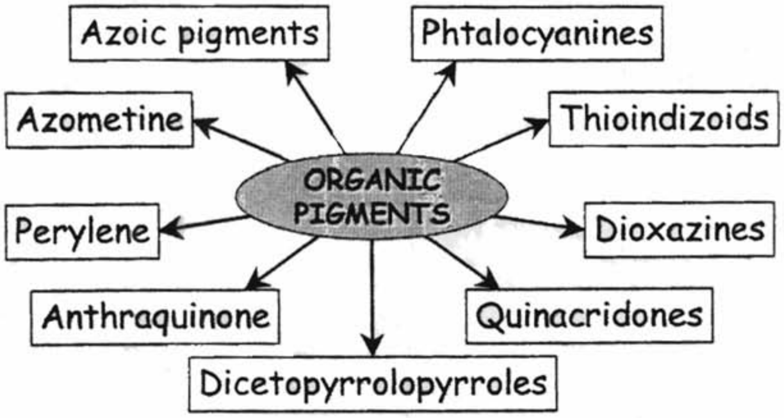

STABILISERS for Chlorinated polymers
Ion and mineral exchangers
Mercaptostannic compounds
Antioxidants
Metallic carboxylates
Organic stabilisers
Mixed stabilisers

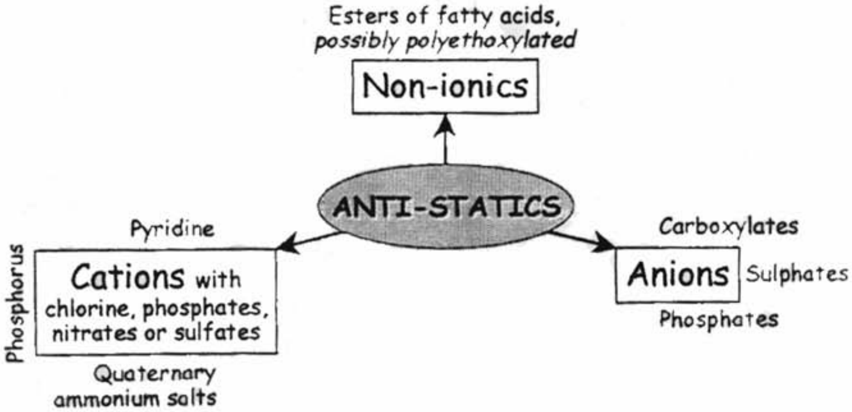

ANTIOXIDANTS
Carbon black
Phenols
Radicular inhibitors
Aminos
Hydroperoxide inhibitors
Thioesters
Phosphites
Metal deactivators
Nitrogen compounds

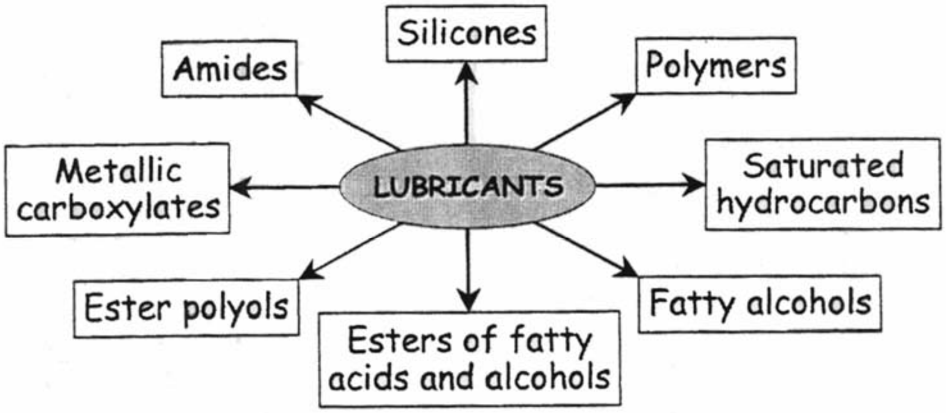

ANTI-UV
UV absorbers
Benzotriazotes
Hydroxybenzo-phenons
Salicates, benzoates, cinnamates, oxalamides, oxanilides
Stable coverings
Protective layers for unsaturated polymers
Quenchers
Frequently nickel complexes
UV absorbing or highly reflective pigments
Carbon black
Titanium dioxides
Radical inhibitors
AES
HALS

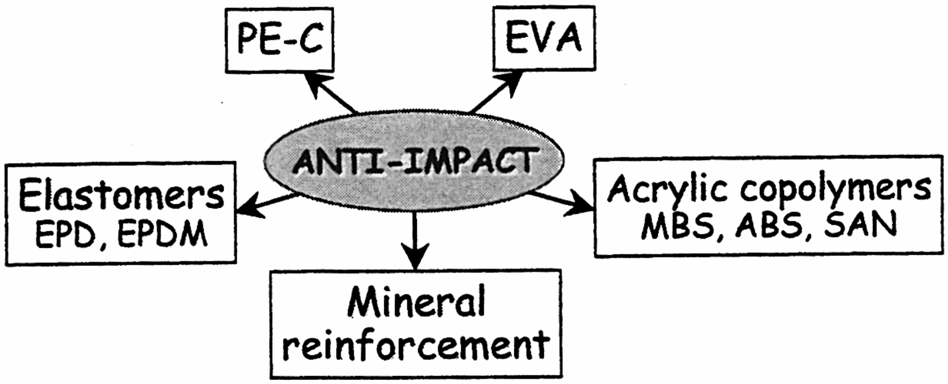

COLORINGS and PIGMENTS
Mineral pigments
Organic pigments
Special pigments
Opal metallic pigments
Fluorescent pigments
Colorings
Anthraquinone derivatives

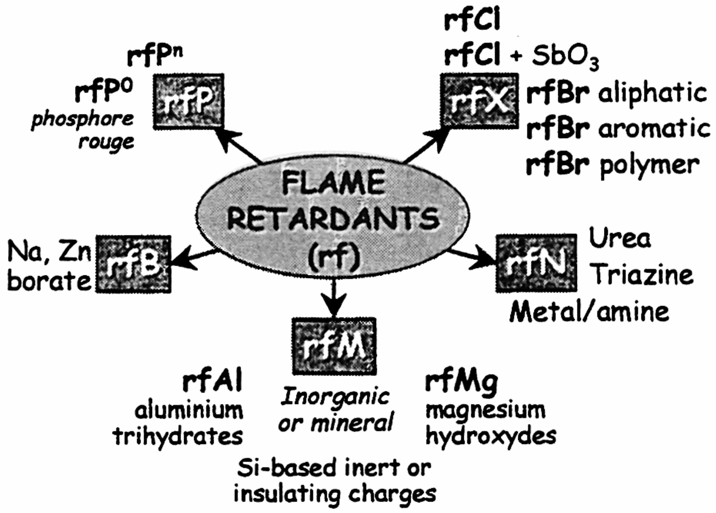

MINERAL PIGMENTS
White
Sulfates and carbonates
Oxides
Others
Black
Blue
Manganese pigments
CoO,Al_2O_3
Na-Al-silicate
$Fe_4(Fe[CN_6])_3$
Orange
Chromates
Antimony
Red and Brown
Chrome oxide pigments
Cobalt pigments
Green
Lead compounds
Ferrous oxides pigments


ORGANIC PIGMENTS
Azoic pigments
Phtalocyanines
Azometine
Thioindizoids
Perylene
Dioxazines
Anthraquinone
Quinacridones
Dicetopyrrolopyrroles


Esters of fatty acids, possibly polyethoxylated
Non-ionics
ANTI-STATICS
Pyridine
Phosphorus
Cations with chlorine, phosphates, nitrates or sulfates
Quaternary ammonium salts
Carboxylates
Anions
Sulphates
Phosphates


Silicones
Amides
Polymers
Metallic carboxylates
LUBRICANTS
Saturated hydrocarbons
Ester polyols
Esters of fatty acids and alcohols
Fatty alcohols


PE-C
EVA
ANTI-IMPACT
Elastomers
EPD, EPDM
Acrylic copolymers
MBS, ABS, SAN
Mineral
reinforcement


rfP^n
rfP^0
phosphore
rouge
rfP
rfCl
rfCl + SbO$_3$
rfX
rfBr aliphatic
rfBr aromatic
rfBr polymer
FLAME
RETARDANTS
(rf)
Na, Zn
borate
rfB
rfN
Urea
Triazine
Metal/amine
rfM
rfAl
aluminium
trihydrates
Inorganic
or mineral
rfMg
magnesium
hydroxydes
Si-based inert or
insulating charges

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