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## **STUDY OF LINSEED OIL POLYMERISATION FOR OPERA RPC'S**

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## 1. INTRODUCTION

The Resistive Plate Chambers (RPC) will be part within OPERA project at Gran Sasso. The electrodes of a RPC are made of 2mm bakelite plates spaced by 2mm. The internal surface of these electrodes must be as smooth as possible in order to increase the signal to noise ratio. For years, a good quality surface was achieved in an efficient and inexpensive way by depositing a thin film of linseed oil on the bakelite internal surface of each RPC. An air flow blown for several days through the chamber at room temperature insured the polymerisation of the oil. This procedure has proven efficient but last year different RPC died due to uncompleted polymerisation of the oil. At the BABAR experiment, for example, many chambers were stopped and dismantled because of detrimental effects induced by the unpolymerised linseed oil.

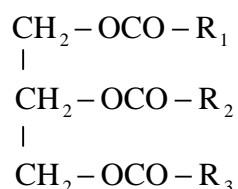
The aim of this work was to review the polymerisation process of the drying oils and to test and characterise the behaviour of different oils, from different suppliers and batches. Different characterisation methods were used as well as different drying conditions. Conclusions were drawn on the necessary quality of oils, on their methods of test and polymerisation.

## 2. GENERALITIES

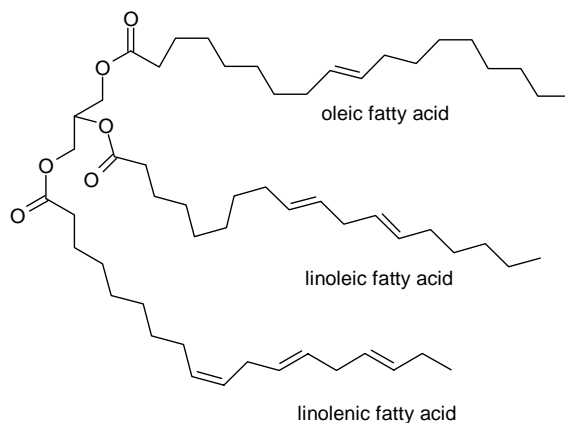
### 2.1 Natural drying oils

A drying oil can be defined as a liquid vegetable oils that, applied in thin layers to a non-absorbent substrate, will dry in the presence of air to form a hard film, non melting and usually insoluble in organic solvents. For example, Tung oil, Oiticica oil, soybean oil, fish oil, castor oil, etc. The linseed oil is quantitatively the most used natural drying oil. The use of the oil in coatings was mentioned by Ludius in 63 BC.

The chemical composition of a drying oil consists basically of triglycerides which structurally are triesters of glycerol and different fatty acids composed of a mixture of saturated and unsaturated acids (see the formula below). The drying characteristic is related directly to the number of ethylene groups contained by the fatty acid. These fatty acids which come from  $R_1$ ,  $R_2$  and  $R_3$  group defined on the figure below, are constituted by 18 carbon atoms with one to three unsaturations.



The most important acids are given in the Table 1.



Example of a triglyceride containing three fatty acids.

| Fatty acid                                | Formula   | Number of double bonds          |
|---|---|---------------------------------|
| Stearic                                   | $\text{CH}_3 - (\text{CH}_2)_{16} - \text{COOH}$  | 0                               |
| Oleic                                     | $\text{CH}_3 - (\text{CH}_2)_7 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOH}$   | 1                               |
| Linoleic                                  | $\text{CH}_3 - (\text{CH}_2)_4 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOH}$                                   | 2                               |
| Linolenic                                 | $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOH}$ | 3                               |
| Eleostearic<br>Mainly present in tung oil | $\text{CH}_3 - (\text{CH}_2)_3 - (\text{CH} = \text{CH})_3 - (\text{CH}_2)_7 - \text{COOH}$   | 3<br>(with conjugated position) |

Table 1 – Fatty acids usually presents in oils.

The average composition of a linseed oil is presented in Table 2

| Fatty acid | Number of double bonds | Quantity |
|------------|------------------------|----------|
| Stearic    | 0                      | < 10%    |
| Oleic      | 1                      | 10-34%   |
| Linoleic   | 2                      | 12-24%   |
| Linolenic  | 3                      | 35-71%   |

Table 2 – The average composition of a linseed oil.

Chemically, the oils used for coating compositions contain a number of ethylene groups to which they owe their drying ability. The ultimate quality of the dried film is a function of the degree of unsaturation. This is the most important requirement and it can be

evaluated by the iodine number (or Wijs' index) or, in certain cases, by the refractive index. Therefore, the natural oils have been classified according to the iodine number:

Drying oil  $I_i > 140$

Semi-drying oil  $I_i = 125 \div 140$

Non-drying oil  $I_i < 125$

In the case of the linseed oil, the iodine number is between 170 and 190. So, it is a drying oil.

The commercially available linseed oils are submitted usually to a quite complex process of purification and to different proprietary pre - treatments. As a function of the thermal treatments applied, the linseed oil is sold under the label "boiled", "blown", "stand - oil", etc. A thermal treatment leads to an increased ratio of conjugated double bonds and therefore to an increased polymerisation rate. Addition of different metal catalysts e.g. organic salts of Ti, Zr, Mn, etc., known as "driers" or "siccatives" accelerates the drying process. Metal catalysts promote the formation of peroxide radicals which initiate the auto oxidative process - see schema below. They shorten the induction time of the drying process and accelerate the rate of oxygen absorption. It was suggested that driers enter into a secondary reaction, lowering the activation energy required to form and decompose the peroxides. For instance, the Cobalt based drier formed a complex with the unsaturated ester, which resulted in an order of magnitude decrease in the energy of activation for oxygen uptake by the ester.

In order to prevent the start of the polymerisation in the storage containers, antioxidants (often having a phenolic structure) are added. When in contact with oxygen, the polymerisation process starts after the consumption of these antioxidants. In fact, the drying process is a result of polymerisation induced by the action of atmospheric oxygen (auto oxidation or oxidative polymerisation).

## **2.2 Oxidative polymerisation**

Naturally occurring glyceride esters used for coating compositions are highly unsaturated. On exposure to air, these alkenes undergo crosslinking by polymerisation and the atmospheric oxygen plays an important role in this process.

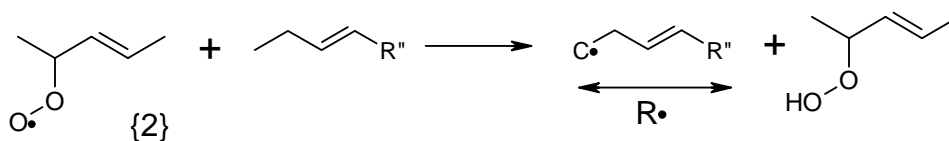
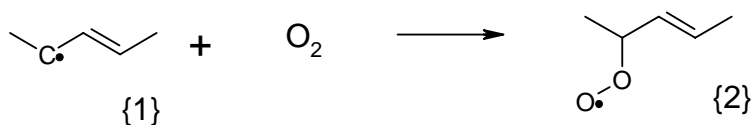
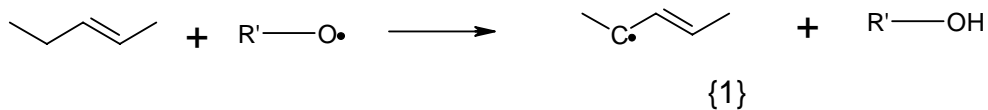
The overall reaction proceeds through initiation, propagation and termination mechanisms (see the figure below). In the initiation step, naturally present hydroperoxides decompose to form free radicals. This step can be catalysed by the inclusion of driers or the application of heat. Initially, these highly reactive free radicals react with antioxidants. Once the antioxidants are consumed, the free radicals can react with the fatty acid chains of the drying oil. Propagation then proceeds by abstraction of hydrogen atoms on the methylene groups between double bonds. Crosslinking proceeds by radical-radical termination reactions. These combinations may consist of C-C bonds, ether bonds or peroxide bonds. The ratio of C-C / ether / peroxide linkages may be related to the concentration of oxygen present during film formation and cure temperature.

The reactions taking place during the drying process are complex. Evaluation of individual mechanisms is difficult since many reaction steps occur simultaneously. The amount of oxygen absorbed increases rapidly in the early stages of film formation and reaches a maximum when the film starts to be formed.

Initiation step

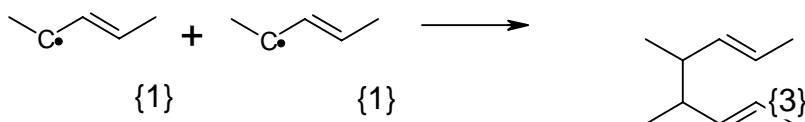


Propagation steps

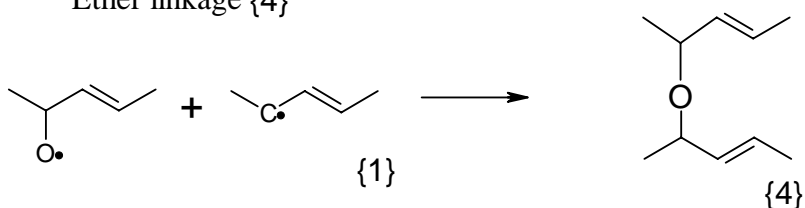


Termination steps

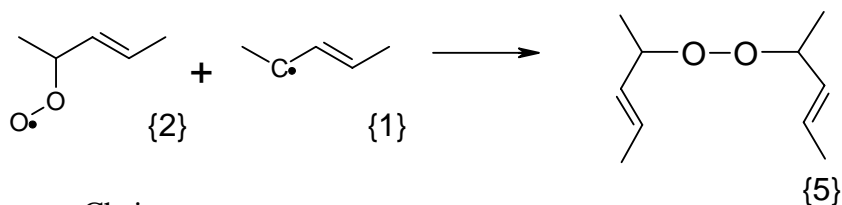
C-C linkage {3}



Ether linkage {4}



Peroxide linkage {5}



Chain



### **3. EXPERIMENTAL**

#### **3.1 Oils – Substance – Materials**

Within the present work were tested six different types of drying oils, as follows:

- ✓ Linseed oil supplied from Sigma Aldrich, Switzerland;
- ✓ Boiled linseed oil supplied from Sigma Aldrich, Switzerland;
- ✓ Boiled linseed oil supplied from Wolf's Linolie-og Trætjærefabrik (linoliefernis), Denmark– named below Linoliefernis;
- ✓ Tung oil supplied from Sigma Aldrich, Switzerland;
- ✓ First sample of linseed oil supplied by the OPERA team in May 2001 – named below OPERA 1;
- ✓ Second sample of linseed oil supplied by the OPERA team in November 2001– named below OPERA 2.

For several tests the oils were previously filtered; for other tests the oils have been used directly from the received bottle.

Appendix 1 presents the certificates of analysis of each linseed oil used for tests, when available.

The solvent used was chloroform p.a., as recommended in the literature

Small plates of Bakelite (70x30mm) provided by OPERA team - i.e. the same type used for RPC's chambers production - were used for tests.

#### **3.2 Unsaturation**

The measurement of the degree of unsaturation was realised using the method of Wijs's Index. It is defined as the mass on iodine expressed in cg consumed per gram of oil (see the method procedure in appendix 2). The evaluation of how the time and the temperature affect the unsaturation level was performed using Wijs's Index.

#### **3.3 Estimation of the polymerisation energy**

Estimation of the reaction energy for film formation was realised using the Differential Scanning Calorimetry (DSC) technique. The apparatus was a Setaram DSC 92. Samples of approximately 30 mg of oil (non filtered) were used for these measurements. Capsules of aluminium were used for all trials. When working in atmosphere of pure nitrogen the capsules were closed and when working in an atmosphere of a mixture of nitrogen and 20% oxygen the capsules were left open. All measurements examined the oils in the interval from 25°C to 190°C; the heating rate was always 10°C/min.

#### **3.4 Film deposition on Bakelite**

The oils were deposited on the Bakelite plates by immersion, after a previous cleaning with chloroform. In order to obtain a very thin film the oil was diluted in chloroform at various concentrations. The plates were left drying at an angle of ca 45° in different environments, in order to see their effect on the drying time and the surface quality.

#### **3.5 Drying Time**

Evaluation of the drying time defined as the Dry-To-Touch Time was carried out according to ASTM D1640 (appendix 3).

### 3.6 Surface Quality

Surface quality is said to be good when the surface is completely smooth and is considered unacceptable when irregularities are observed. By nature this is a subjective parameter; therefore, photos have been taken of various plates to document the conditions of the surfaces. The surface quality has been evaluated both visually and using different types of microscopes (optical and scanning electron microscope - SEM), see appendix 4 and 5.

### 3.7 Deposit thickness

The deposit thickness was measured using a SEM.

### 3.8 Refractive index

This number is a dimensionless quantity that is related to the ratio of the speed of light in air (or vacuum) to its speed in another medium.

It is useful in detecting adulteration in oils containing substantial amounts of conjugation, such as Tung and Oiticica oils. Since the refractive index varies with iodine value, it can be used in certain situations for a quick approximation of iodine index (ASTM D 555).

## 4. RESULTS AND DISCUSSIONS

In order to evidence the influence of the deposition parameters on the quality of the final polymerised oil layers, all the available oils were used for coatings. The following parameters were checked:

- Pre-filtration
- Environmental atmosphere
- Temperature
- Oil-solvent ratio

It is to be noticed that the as-received Bakelite plates, uncoated, presents different surface defects and non-uniformities that justify the necessity of a coating layer deposition, apart its intrinsic quality as quencher. For comparison, samples of “good” or “bad” quality plates for OPERA are presented (see appendix 4 for optical photos and appendix 5 for SEM photos). The microscopic techniques (optical and SEM) are more precise and accurate as compared to a simple visual. It is to be noticed, also, that the pictures in the appendix 5 are focused mainly on defect areas corresponding to each deposit types.

The step of the oil filtration prior its deposition improved the uniformity of the deposited layer mainly for the oil samples which were in contact (even for short time) with air. Within such samples were observed and separated by filtration submillimetric gelified zones where the pre-polymer begin to form. It must be underlined that these zones are very difficult to be observed in situ without filtration. The refraction index of these gels is equal to the oil index thus making them invisible by optical inspection. If the gel fragments are left in oil, the final dried layer will contain small circular areas with “heights”.

A similar effect was evidenced in the case when the oils layers were polymerised or dried – in a free laboratory atmosphere. The “dust” particles are trapped and can be observed within the coating layer; they can also constitute the first polymerisation centers leading to the nonuniformity of the polymerised coating layer.



The effect of the environmental temperature on the drying time and the surface quality during the polymerisation process was studied at 17°C, 22°C and 45°C. For comparison purposes, for each temperature the oils were tested taking into account the following five parameters: open atmosphere; closed atmosphere (desiccators); ventilated oven; unfiltered and filtered oil previous its deposition.

The shortest drying time required for a good polymerisation were obtained at 45°C (see table 3)

|                 | <b>Linseed Oil</b> | <b>Boiled Linseed Oil</b> | <b>Tung Oil</b> | <b>Oil used previously for OPERA</b> | <b>Linoliefernis</b> |
|-----------------|--------------------|---------------------------|-----------------|--------------------------------------|----------------------|
| <b>θ = 22°C</b> | 50                 | 18                        | 20              | 19                                   | 16                   |
| <b>θ = 45°C</b> | 14                 | 12                        | 10              | 12                                   | 12                   |

Table 3 – The influence of the polymerisation temperature on the drying time, in hours.

The variation of the oil-solvent ratio allowed the obtention of different thickness of the final dried layer. Lowering the oil concentration, the fluidity and the wettability of the liquid mixture were improved as well as the final quality of the coating layer (see Table 4 and appendix 5).

|  | Samples prepared in laboratory:<br>Filtered<br>θ = 45°C<br>Desiccators<br>(oil-solvent) % by volume |                                      |   |   | Samples received from OPERA projects          |  |   |
|--|---|--------------------------------------|---|---|---|--|---|
|  | <b>OPERA 1<br/>30 - 70</b>  | <b>OPERA 1<br/>15 - 85</b>           | <b>Boiled<br/>Linseed oil<br/>30 – 70</b>                         | <b>Boiled<br/>Linseed oil<br/>15 – 85</b> | <b>“bad”<br/>coating</b>                      | <b>“good”<br/>coating</b>                      | <b>Bakelite<br/>without oil</b>                   |
| <b>Comments<br/>on surface<br/>quality</b> | Smooth<br>but<br>wetting<br>problems  | Smooth<br>but<br>wetting<br>problems | Smooth<br>but<br>wetting<br>problems,<br>with minor<br>impurities | Good<br>deposit                           | Dusty,<br>wetting<br>problems,<br>non-regular | Wetting<br>problems<br>and minor<br>impurities | Defects:<br>Holes,<br>cracking<br>lines,<br>bumps |
| <b>Film<br/>thickness<br/>[µm]</b>         | ≈ 6   | ≈ 5                                  | ≈ 6   | ≈ 4                                       | ≈ 2   | ≈ 2  | Not coated  |

Table 4 – Comments on linseed oil coatings vs. depositing parameters.

The unsaturation grade of the studied oils was measured using the Wijs’ method. The values obtained are presented in Table 5. The higher unsaturation grade leads to a faster polymerisation rate. The Wijs’ index served to order the studied oils as a function of their unsaturated bonds content. For OPERA 2 oil only, due to the presence of a solvent, confirmed also by viscosity measurements, its measured index is not representative for the undiluted oil.

|                    | Linoliefernis | Boiled Linseed Oil | Linseed Oil | OPERA 1 oil | Tung Oil | OPERA 2 oil * |
|--------------------|---------------|--------------------|-------------|-------------|----------|---------------|
| <b>Wijs' Index</b> | 180           | 172                | 170         | 128         | 125      | 87*           |
| <b>Rank</b>        | 1             | 2                  | 3           | 4           | 5        | 6*            |

\*The OPERA 2 oil as received is diluted in a solvent

**Table 5 – The iodine indexes of the studies oils.**

As the Wijs'index values obtained for the Tung Oil and OPERA 1 oil were surprisingly low - below the accepted limit of a drying oil and below their specification – a too long storage time accompanied by the contact with the atmospheric oxygen was considered as a possible cause. Therefore, an experiment was carried out to simulate the suspected reason for the small iodine values. Because the freshly supplied Tung oil has its index close to that of the available Linoliefernis, this last one was chosen for the experiment. It was kept in air for different times and temperatures and its iodine index was immediately measured. The results are presented in table 6.

| Linoliefernis      | Start Value | 24h at 45°C | 24h at 45°C + 24h at 20°C | 24h at 45°C + 72h at 20°C |
|--------------------|-------------|-------------|---------------------------|---------------------------|
| <b>Wijs' Index</b> | 180         | 150         | 150                       | 120*                      |

\* a film was formed on the surface, Wijs' Index was measured on a sample taken from the liquid beneath this film.

**Table 6 – The Wijs'index decrease as a function of air contact time and temperature.**

The alteration of the unsaturated bonds content is obvious for the oils in contact with oxygen, even for relatively short periods of time. This can explain the small values found for Tung oil and the relatively old sample of OPERA 1 oil, as was supposed.

The relative reaction energies were measured by DSC method, taking as reference the oil OPERA 1: its reaction energy was considered 100. Each studied oil was measured in inert atmosphere and in air. Each DSC run was repeated in order to evidence the eventual post effects. The results are summarised in Table 7.

|                     |                     | The relative reaction energy |                    |             |             |          |              |
|---------------------|---------------------|------------------------------|--------------------|-------------|-------------|----------|--------------|
|                     |                     | Linoliefernis                | Boiled Linseed Oil | Linseed Oil | OPERA 1 oil | Tung Oil | OPERA 2 oil* |
| Nitrogen Atmosphere | 1 <sup>st</sup> run | 0                            | 9.8                | 10.1        | 43.7        | 0        | 0*           |
|                     | 2 <sup>nd</sup> run | 0                            | 0                  | 0           | 0           | 0        | 0*           |
| Air Atmosphere      | 1 <sup>st</sup> run | 339.1                        | 249.5              | 220.1       | 100         | 67.2     | 84*          |
|                     | 2 <sup>nd</sup> run | -                            | 272.8              | 340.4       | 82.5        | 102.0    | 0*           |

\*The OPERA 2 oil as received is diluted in a solvent

**Table 7 – The relative reaction energies as resulted from DSC measurements.**

It can be observed from Table 7 that the reaction is negligible in nitrogen; the small thermal activity recorded can be attributed to the presence of traces of oxygen introduced during samples preparation. In air atmosphere, the most reactive appeared the linoliefernis

together with the boiled linseed oils, as expected. The second run evidences the continuation of the polymerisation in the presence of oxygen.

The DSC measurements confirm the experimental observations. Very important, these measurements confirm also the same classification order of the oils reactivity obtained from the iodine index measurements. From the point of view of practical application, the measure of the Wijs' index is a rapid way for the evaluation of the polymerisation potential of an oil and hence of its expected quality.

## **5. CONCLUSIONS**

The linseed oils are siccativ substances composed from different unsaturated acids able to polymerise in presence of oxygen. As all the natural products, their composition varies from batch to batch. Their treatments and additives are often proprietary. Well established technical specifications and acceptability tests are mandatory for a good and reproducible quality of the final coating obtained.

The Wijs' index method allowed the classification of oils to be established. The results were confirmed by DSC method. The contact between oils and air prior the oil deposition is detrimental to the final quality and also for the polymerisation degree of the final coating layer. The polymerisation potential of an oil can be evaluated from its Wijs' index (iodine index). For each batch of freshly received linseed oil and also prior the reuse of an oil mixture, the measurement of the Wijs' index is highly recommended.

The antioxydant substances (stabilisers, containing often aromatic rings) present in the as received oils are eliminated prior the polymerisation process starts. Thus, phenolic residues identified on certain RPC chambers can have their origin in such substances.

Different drying oils and conditions were used in the laboratory for coating the Bakelite support. The best results were obtained, in laboratory conditions, using a diluted solution (15% of boiled linseed oil or linolieferniss and 85% chloroform); the temperature was 45°C and time in air flow contact 12 hours.

A constant and high flow rate of air must be present over the entire polymerisation process.

Viscosity measurements are useful for a correct appreciation of the constancy of the oil/solvent ratio during the repetitive deposition processes using a closed circuit.

The refractive index measurement, despite some positive references in the literature is not enough sensitive for the present type of application.

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