

## The Use of Saturated Plant Oils in the Synthesis of Film-Forming Materials

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According to the performance properties of the bitumen-polymer coatings we assumed the need of their physico-chemical modification: to plasticize and exception thus oxidative degradation, i.e. premature aging, and in order to achieve high adhesion strength properties. Film-forming materials based on saturated plant oil and elemental sulfur possess needed bifunctionality. The complex of investigations to determine the degree of physical and chemical interaction between sulfur and saturated plant oil during heat treatment, mechanical activation and oxidation was carried out. The optimal and limiting amount of sulfur entrained into oil was determined. The basic chemical reactions that take place with the participation of sulfur in implementation of the process at low temperatures were clarified. It was found, that at relatively low temperatures (in the physico-chemical treatment) sulfur gives greater flexibility and ductility.

**Key words:** paints, additives, film-forming materials, sulfur, polyfunctional modifiers

Initially in the paint industry there were used only unsaturated seed oils. If a thin layer of paint is applied in any surface, it starts to absorb oxygen from air that makes a solvent resistant elastic coat. This property is seen in several oils, particularly in linseed oils, that are used in the manufacture of printing inks, linoleum, tissue coated with drying oil etc. The amount of these oils was not determined by studying the structure and chemistry of film formation and also aren't the results of any theory. It is just the collection of empirical data gained by similar crafts.

According to their properties seed oils are classified into three groups: drying, semi-drying

and non-drying. Initially, it was accepted to use only drying seed oils to obtain high-quality paint and varnish materials. Semi-drying seed oil was used as impurities or additives that were decreasing the cost and non-drying seed oil-as a useless material in paint industry<sup>1-3</sup>.

The situation changed radically with the advent of oil modified with alkyd resins and the subsequent development of significant research in this area. It is now possible to obtain some kind of paints, from almost all known seed oils<sup>4</sup>. Evaluation of seed oil as a part of paint material should be based on scientific researches, however some details are not enough certain.

The purpose of first part of this research is to learn the interaction processes between sulfur and saturated plant oil. After that it is necessary to create production technology of film-former, plasticizer and antioxidant in bituminous paints and varnishes. The main objectives are:

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- a) To compare the various ways of involving sulfur to the oil;
- b) To research the influence of sulfur to the properties of sulfur-oil compositions;
- c) To reveal the influence of various factors (amount of added sulfur, temperature, time of thermal and mechanical activation treatment) on the properties of sulfur-oil composition.

### Methodics

Processing with sulfur is used much less than polymerization and oxidation methods, particularly, in the manufacture of overshoes varnish. Initially, the oil is usually oxidized, and then powdered sulfur is treated.

As a basis of film-former material saturated plant oil (related to weak drying oil) was chosen. It is necessary to mix with drying oils (hempseed, linseed, etc.) in order to be able to use it as a film-forming substance<sup>1-5</sup>. The oil is characterized by the presence of large amounts of fatty acids with a double bond. Characteristics of saturated plant oil are shown in Table 1.

According to literature data, the modified components should have properties of plasticizing and have to withstand thermo-oxidative destructions of paint-and-lacquer coatings (PLC)<sup>6</sup>. By another words components have to function as inhibitor-antidestroyer during production of paint-and-lacquer materials (PLM or coatings). All above mentioned features have sulfur.

Sulfur with regard to its content may form associated with the existing particles of the dispersed phase spatial structures due to the formation of complex structural unit (CSU) may form space structures, if certain content is chosen. So the property of materials would be determined by this new spatial conjugating structure. Even at low concentrations this addition may bring structural effects, at high concentrations plasticizing and vice versa. In the first case, obviously, it must be due to the fact that the content is high enough above defined that mean additive cannot be distributed in a dispersing medium, and will act as hinges in shear. In the second case, when the content is certain, it will be sufficient to form an independent or conjugated to the particles of the dispersed phase of the spatial structure. Thus, it is necessary to solve the effective introduction of sulfur into saturated plant oil, which

yields stable compositions.

Despite the large number of papers devoted to the behavior of sulfur, a single point of view on the processes, occurring at the same time, does not exist. Reaction of Sulfur with oils may occur at different temperatures. During high temperatures (above 180-200 °C) the dehydrogenation process starts, which continues with the release of hydrogen sulfide. In low temperatures (120-150 °C) sulfur reacts with fatty acids without releasing hydrogen sulfide. By the way the element is in three main states: chemically bounded, dissolved and dispersed, and the distribution between the different forms of sulfur depends on the conditions of introduction, the properties of the oil, the amount of sulfur input. Various researchers have proven the presence of sulfur in one form or another in almost all classes of hydrocarbons. We consider that during synthesis of the plasticizing agent PLM, bounded sulfur exists in the form of polysulfide chains<sup>6-7</sup>.

To obtain the most stable systems, in which most parts of sulfur is in bounded condition, the process has to be carried during long period. On the binding step of sulfur the role of contact condition and amount of sulfur is also important. It is presumed that sulfur introduced to the structure of fatty acids is the good modifier of obtained plastic properties and comparatively more oxo-thermo resistant.

It is well known, for modified material to have polymeric properties it is necessary to create a polymer framework in substance space, which is possible with a critical concentration of forming structure. If the concentration of polymer is further increased in composition, overlapping of particles of dispersed phase starts. By another words, modification of saturated plant oil and sulfur may be characterized by two critical concentric structures: lower and higher. These concentrations are determined on the basis of theory of the stability of colloidal systems<sup>8</sup>.

On the dispersed particles of polymer solution some repulsive forces are acting. These forces are the result of decreasing entropy in macromolecule chains, restriction of dispersed particles on the surface and attractive forces [8]. In case of small concentration of polymer modifier (sulfur) in saturated plant oil prevails repulsion forces. Upon reaching the minimum critical

## Saturated plant oil modification by the use of sulfur

The influence of all three factors is observed during interaction of saturated plant oil and sulfur. Addition of less than 10% of sulfur has no significant effect, the influence of other factors are also minimum. Adding more sulfur has a

### Saturated plant oil according to GOST

Physical and chemical parameters	Values
Odor and taste	Peculiar to saturated plant oil, free of different smells
Density at 20 C, g/CM3	0,908-0,915
Number of acidity (no more than)	4,0
Iodine number	19
Flash Point by Martens-Pensky, C (no less than)	230
Pour point, C	from -4 till -10
Index of refraction, n40D at 20°C	1,472-1,476

Component ratio of film-former: PFM, %	Hardness with ISO 15184 scale, points	Adhesion, points	Bending with GOST 6806-73[9], points	Hardness units.
1:99	0	4	2	0,06
5:95	5	1	1	0,17
10:90	5	1	1	0,14
15:85	5	1	1	0,10

Component ration of film-former: PFM, %	Hardness with ISO 15184 scale, points	Adhesion with ISO 4624-78, kgf/cm <sup>2</sup>	Adhesion, Bending with points GOST 6806-73, mm	Hardness units	
1:99	0	21	4	2	0,24
5:95	5	19	2	1	0,29
10:90	5	18	1	1	0,22
15:85	5	16	1	1	0,16

Time, min.				0	30	60	90	120	150	180	210	240	270	300
Component , % ratio, Film- former: modifier	10:90	Charge density, MV	3 <sup>rd</sup> Day	-130	-140	-150	-200	-190	-280	-160	-160	-160	-160	-160
			5 <sup>th</sup> Day	-360	-350	-350	-340	-330	-330	-320	-320	-310	-310	-310
	15:85		7 <sup>th</sup> Day	-360	-360	-360	-360	-350	-330	-270	-270	-270	-260	-260
			3 <sup>rd</sup> Day	-370	-370	-370	-370	-340	-340	-340	-340	-350	-350	-350
			5 <sup>th</sup> Day	-330	-270	-230	-230	-220	-210	-200	-200	-190	-190	-190
			7 <sup>th</sup> Day	-160	-160	-170	-150	-140	-170	-230	-250	-270	-270	-270

significant influence on its content, while an effect of mechanical activation and heat treatment time are seen as well

It is found that by adding a small amount of sulfur (5%) the content of unsaturated compounds are not changed significantly and signals of crystalline sulfur are not observed. If the amount of sulfur is increased up to 15%, its

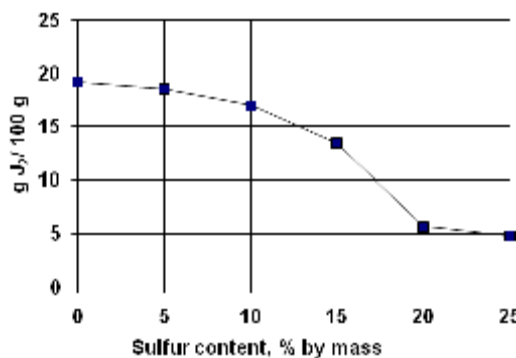
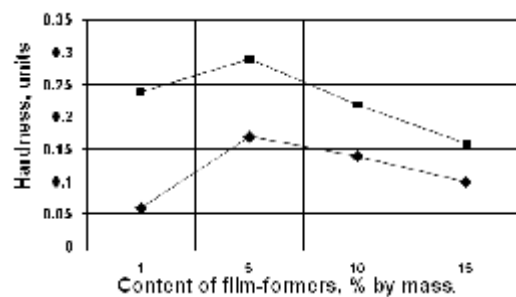


Fig. 1. Change of iodine value in saturated plant oil based on the content of added sulfur



(A)

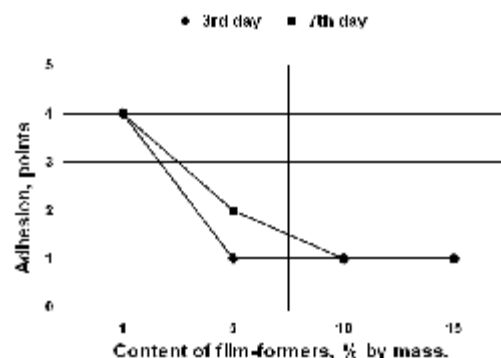
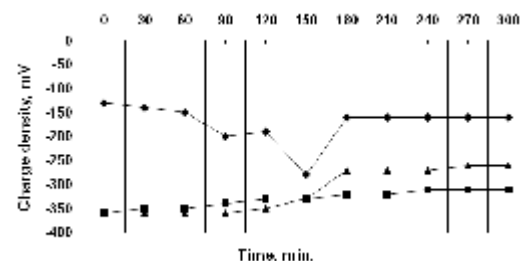
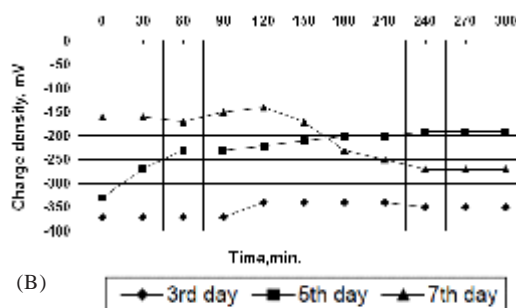


Fig. 2. Change of hardness (a) and changes in adhesive properties (b) based on film-former systems: PFM over time



(A)



(B)

Fig. 3. Electrochemical resistance of coating systems of film-formers : PFM with a component ratio of a – 10:90, b - 15:85 over time

and amount of dispersed medium. Only after this step interaction of sulfur with dispersed phase (asphaltenes part of bitumen) can be observed. Interaction with asphaltenes will lead to the introduction of sulfur in the crystal lattice of supramolecular asphaltene associates, presumably without forming a chemical bond. Sulfur introduced during the subsequent heating can interact with the asphaltenes to form a chemical bond, or can be released from asphaltenes and interact with the dispersion medium.

Thus by mixing saturated plant oil with sulfur a homogenous mixture of carbon-sulfur is obtained, that preserves stability over time. This indicates the compatibility of sulfur with unsaturated acids.

Decisive influence on the interaction of sulfur with hydrocarbons makes a temperature regime. Interaction are proceeded differently at low (about 120-150 °C) and high (more than 160-180 °C) temperatures.

Cyclic structures (clusters) of sulfur are enough stable at a temperature less than 120 °C. At higher temperatures (more than 140 °C) clusters are splatted with a formation of radicals, containing of sulfuric atoms and then depending on the nature of feedstock, it is just connects to alkene type of hydrocarbons or dehydrogenation of hydrocarbon oil residuals with excluding hydrogen sulfide takes place. The presence of electro-, nuclei- filing agents makes splitting of sulfur clusters much easier at low temperatures (120-140 °C).

During sintering of saturated plant oil and sulfur (in an amount of 20%) the degree of dispersion (the amount of unreacted sulfur) is visually determined. The results of dispersion degrees are shown in Table 2.

As the product of sintering saturated plant oil with sulfur the time interval of gelation is determined, which is the result of polymerization and compaction reactions. It is important that film-former knew how quickly oil is polymerized, because generally polymerizations continue till initial point of gelation. Results of the research on time-interval of gelation are following: adding sulfur up to 25 per cent leads to gelation time decrease drastically.

As a result of complete gelation a soft sticky viscous mass (very similar to a gel) forms, which is difficult to remove and dissolve in organic

solvents. This product has no practical interest, so it is recommended not to bring oil to complete gelation. From Table 2 it can be observed that saturated plant oil with a content of 25% is almost instantly gelled. Therefore, sulfur with a content of 20% is the optimum additive to saturated plant oil as a film-former and for creating compaction.

#### **Improvement the properties of polyfunctional modifier (PFM) within addition of film-former based on saturated plant oil and sulfur**

Physical and chemical properties of synthesized film-former (based on saturated plant oil and sulfur) with PFM which has strong adhesive properties need to be combined. Film-former based on saturated plant oil and sulfur was combined with a modifier. Results and visual evaluation: Dark brown color is given to solution by film-former based on saturated plant oil and sulfur (as a result of their fusion formed dark brown colored solution). Transparency of solutions and absence of any precipitations is due to complete distribution and interaction of all components in the film-former system: PFM.

To evaluate the adhesion strength and plastic properties, studies were carried on obtained coatings. Results of coatings for third day are presented in Table 2

The results of physical and mechanical studies of film-former systems: PFM presented in Table 3

For clarity data from tables 2 and 3 is presented graphically in figures 2 a and b, respectively.

Samples with the PFM content of 90, 85% and 10-15% film-formers were selected. The selected samples vary with a strong adhesion and hardness. Moreover they have good plastic properties. An increase in hardness from the third to the seventh day is observed.

Thus, the film-forming material based on saturated plant oil and sulfur gives films strength. The difference of PLM based on film-former and PFM is in having high chemical resistance. Also they are resistible to atmosphere, elastic and have good adhesion. Besides they dry fast and has high protective properties.

Evaluation of protective capability to electrochemical corrosion coatings based on film-formers and modifier (PFM)

According to component ratios of film-

formers and modifier 10:90 and 15:85 respectively, resistance of coatings to the electrochemical corrosion was observed. The results of observation are given below in Table 4

For clarity, the degree of occurrence of electrochemical corrosion and the corrosion resistance of coatings in time given by Table 5 are presented graphically in Fig. 3 a and b.

These electrochemical experiments let us to make observations about the strength and stability of coatings based on film-makers and modifiers with respect to corrosion environment over the time<sup>10</sup>.

Physical, chemical and electrochemical observations done on the dynamic of 3<sup>rd</sup>, 5<sup>th</sup> and 7<sup>th</sup> day shows the mutual complement of each other as a film-former, as well as modifying addition. Especially plastic properties which are missed in modifiers will be completed by film-former and vice versa. Also the improvement of both adhesion forces and protective properties from corrosion are observed.

PLM based on PFM and film-former based on saturated plant oil and sulfur is very transparent solutions, which indicates of full mutuality and mixing of all components. PLM with a content of 85%-90% PFM and 15%-10% of film-former are very different in high adhesion value (1 point), with a hardness of 0.16-0.22 units and bends around 1mm. Besides it is enough resistant to corrosive environments.

## CONCLUSION

Based on previously conducted studies on the performance properties of the bitumen-polymer coatings, namely their adhesion and strength properties, it can be concluded on the need of their physico-chemical modification: 1) to plasticize and exception thus oxidative degradation, i.e. premature aging; 2) in order to achieve high adhesion strength properties.

According to the available prerequisites film-forming materials based on saturated plant oil and elemental sulfur possess needed bifunctionality. The complex of investigations to determine the degree of physical and chemical interaction between sulfur and saturated plant oil during heat treatment, mechanical activation and oxidation was carried out.

Using the results of studies of the physical modification of saturated plant oil by sulfur, optimal and limiting amount of sulfur entrained into oil was determined, that is 20%.

The basic chemical reactions that take place with the participation of sulfur in implementation of the process at low temperatures (120-150) were clarified. It was found, that at relatively low temperatures (in the physico-chemical treatment) sulfur gives greater flexibility and ductility.

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