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Improvement of the physico-chemical characteristics of sunflower oil through thermo-chemical processing and its use in the anticorrosive paints

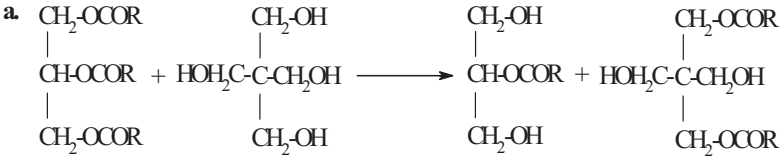
Sunflower oil, soya oil and maize oil are semi drying oils but they cannot be used in the paint industry without being processed first. There are different methods to process these oils in order to improve their physico-chemical characteristics. This article deals with the transforming process of the sunflower oil into PENTOLS. This consists in treating the sunflower oil with pentamaleinat in order to increase the number of the double bounds to the molecule of the triglyceride. Changing the stereo chemical structure of the molecule enables this oil to become drying, obtaining the characteristics of the linseed oil. Linseed oil is widely used in industry of the film forming substances making up to 25% at same paint recipes. Linseed oil is part of group of oils called drying oils a characteristic which gives it the priority in usage due to the great number of its double bonds. Recently there is a shortage of linseed oil in global scale. The sunflower treated with 7% pentamaleinat was used as a replacement of the polymerized linseed oil at the anticorrosive paints.

INTRODUCTION

Sunflower oil is semi drying oil but it cannot be used in the paint industry without being processed first [4], [7], [10]. There are a lot of reactions that happen during the thermo-chemical processing of sunflower oil affecting double bonds and ester groups [9]. The thermo-chemical processing of sunflower oil, transforming it in pentols (alkyd resins maleic-penta) includes the following chemical reactions:

Alcoholysis obtaining polyalcohols partly esterified.

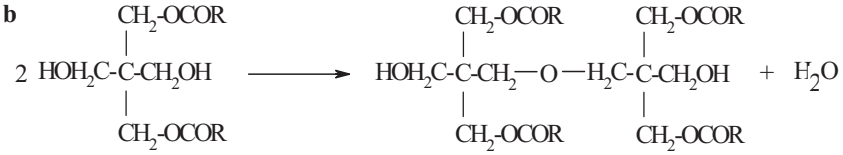
a.



(1)

Oil Pentaerythritol Monoglycerid Pentaerythritol diester

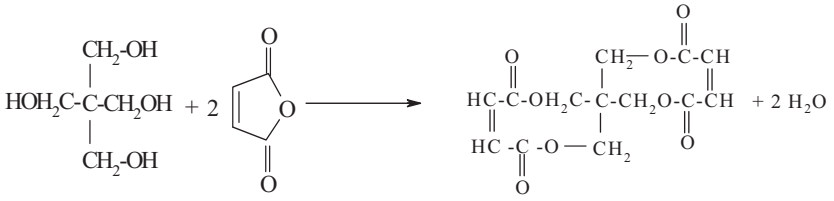
b



(2)

Pentaerythritol diester

Pentaerythritol diester reacts further forming high esters of polyalcohols. The reaction is complicated, but the reesterification process of the dipentaerythritol is considered as a reaction between pentaerythritol and the maleic anhydride, thus obtaining alkyd resins maleic-penta (pentamaleinat) [5, 6].



c.

(3)

Pentaerythritol Maleic anhydride Alkyd resins maleic-penta (Pentamaleinat)

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EXPERIMENTAL PART

The experimental work is performed at the apparatus figure 1. In a flask are added sunflower oil pentaerythritol and lead oxide as catalyzer. The mixture is continuously stirred and gradually heated up to 260˚C [10]. The temperature of 240˚C is kept until all the particles of pentaerythritol are totally melted. After this is done the temperature lowered up to 200˚C and maleic anhydride is added in 4-5 portions in order to avoid the violent gas releasing due to water formation. After all the quantity of maleic anhydride is added the temperature is raised again to 240˚C in order to continue the reesterification. The reesterification is considered done when the acidity is < 10mg KOH/g [3]. The temperature is then raised up to 290˚C and kept at this temperature until the viscosity reaches the value 15±2 seconds 25˚C [3].

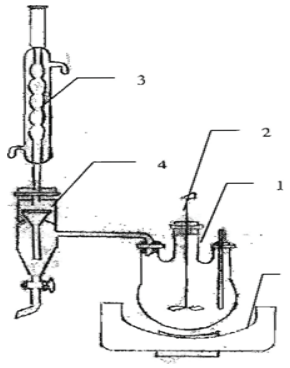

Figure 1

A number of tests of different percentages of pentamaleinat in sunflower oil (300ml) i.e. 5%; 7%; 8%; 9% and 10% are done [2]. The quantity of the row materials for each test, according the reaction 3, is summarized at the table 1.

Table 1 - Tests of sunflower oil with different percentage of pentamaleinat

	Raw materials	Unit	I	II	III	IV	V
1	Sunflower oil	g	276	276	276	276	276
2	Pentaerythritol	g	6.34	8.9	10.2	11.4	12.7
3	Maleic anhydride	g	9.12	12.8	14.7	16.4	18.3
4	PbO	g	0.2	0.2	0.2	0.2	0.2
5	Pentamaleinat	%	5%	7%	8%	9%	10%

RESULTS AND DISCUSION

For the procces of pentols formation the following factors are determined:

a. The determination of the alcoholysis temperature. According to the literature [9, 10] the recommended alcoholyse temperature of the fatty acids with polyalcohols is 240-260°C, since pentaerythritol melts at 230°C a higher temperature is necessary in order to make it possible to react. At 240° the mass is opaque. The full transparency of the mass is reached at 250°, while at 260° it does not change but becomes more fluid. The necessary time is 30-50 minutes. It is kept for 50 minutes at 250°C for better results. In this process polyvalent metals oxide are used as emulsifier mostly PbO. PbO became a soup of Pb (reaction 4), after reacting with the free fatty acids present of the vegetable oils (the allowed limit is 0.5 mg KOH/g oil). Pb soap is a powerful emulsifier.

$$2RCOOH + PbO \rightarrow (RCOO)_2Pb + H_2O \qquad (4)$$

b. The determination of the temperature and the proper time of maleic anhydride dosage. The recommended temperature for the alkyd resins is 180-200°C. Maleic anhydride is added in 4-5 portions (1-1.5g each). After the alcoholysis at 250°C the temperature is lowered up to 200°C and the first portion of maleic anhydride was added. The esterification (reaction 3) led to water releasing in vapor form and temperature decreasing. The temperature is kept constant through continuous warming. The necessary time was 10-15minutes.

c. Time and temperature of esterification. From the experience of production of alkyd resins at Tirana paint factory the esterification temperature of 240°C is chosen. The esterification indicator is the acidity of the mass which is decreased with the time. The acidity determination in time intervals of 0.5-1 h is performed. The reaction ended after two hours when the acidity fell to ≤ 10mg KOH/g. The data of acidity and time of esterification are summarized at the table 2 and figure 2.

Table 2 - Change of the acidity of sunflower oil from the esterification time

	Description of property	Unit	**1**	**2**	**3**	**4**
1	Esterification time	minute	0	60	90	120
2	Acid Value	mg KOH/g	30,013	15	7	0.06

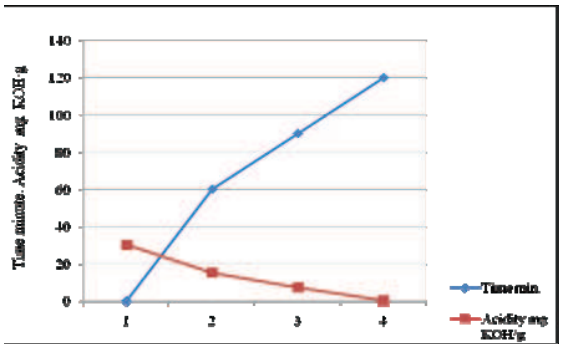

Figure 2 - Change of the acidity of sunflower oil from the esterification time

d. Determination of the temperature and time of polymerization. Linseed oil when used in different paints must undergo to a polymerization process at 290°C until the viscosity reaches the value 15± 2 sec. at 25°C. For sunflower oil are experimented with different temperature according the table 3. The time for each temperature was two hours. Values of the viscosity for each temperature are summarized at the table 3. Knowing that the polymerization happens at lower temperatures too it is experimented at 290°C monitoring the viscosity every hour. It is concluded that the polymerization happened also at 290°C. The relation between temperature and polymerization grade (polymerization grade is determined from the viscosity) is given at table 3 and figure 3.

Table 3 - Change of the viscosity from the polymerization temperature

	Description of property	Unit	1	2	3	4
1	Polimerisation temperature	°C	260	270	280	290
2	Viscosity	seconds	3	7	9	90

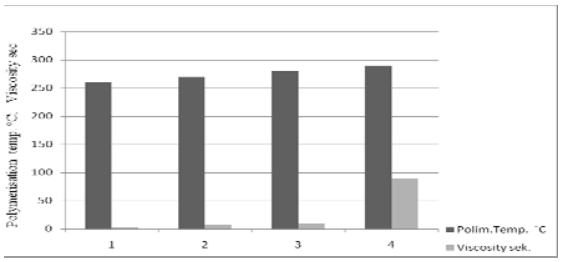

Figure 3 - Change of the viscosity from the polymerization temperature

e. Determination of the percentage of pentamaleinates. Different variations (according Table 1) are experimented. The technological process is exactly applied using optimal parameters getting out from items a, b, c and d. Temperature of alcoholysis 250°C. Time of alcoholysis 50 minutes. Temperature of maleic anhydride dosage 180-200°C. Time of the dosage 15 minutes. Esterification temperature 240°C. Esterification time 2 h. Polymerization temperature 290±2°C. Viscosity measurement first after 2 hours then every 1 hour.

From the experiment it is noticed:

a. It is observed not any difference at the temperature and time intervals of alcoholysis and esterification.

b. There was a big difference (as expected) at the time of esterification.

c. As the quantity of pentamaleinat is increased the viscosity underwent a big increase up to 9% within the same time interval tending toward gelatination. At 10 % it is gelatinized within 6 hours. At the table 4 it is given the change of viscosity in relation with polymerization time and pentamaleinat concentration values.

Table 4 - Change of the viscosity in relation with polymerization time and the percentage of the pentamaleinates

		%	Time of polimerisation h					
			0	2	4	6	8	10
			Viscosity in seconds					
1	Pentamaleinat	**5**	3	3.2	3.7	4	4.2	5
2	Pentamaleinat	**7**	3	5.7	7.2	14.5	-	-
3	Pentamaleinat	**8**	3.2	6	10	17	-	-
4	Pentamaleinat	**9**	3.6	8	12	25	-	-
5	Pentamaleinat	**10**	4	10	20	Gelatination		

Sunflower oil with 7% pentamaleinat turned out to have physico-chemical and technological characteristics almost the same as linseed oil polymerized 15 seconds. This oil is used as a base for the anticorrosive paint producing grey and brown.

f. The Preparation of anticorrosive paints with sunflower oil with 7% pentamaleinat. In laboratory conditions are prepared 0.5kg basic paint components from which the grey and brown anticorrosive paints are prepared.

A. Paint basic components are formulated according to the recipe given at table 5.

Table 5 - Recipe of paint basic components

	Raw materials	Quantity in g
1	Sunflower oil with 7% pentamaleinat	200.35
2	Tung oil	66.1
3	Colophon esterified with glycerin	60.25
4	Calcium rosinat	11.05
5	Phenol formaldehyde resin	17.85
6	Yellow lead oxide PbO	3.6
7	White-spirit	144.3

To prepare the paint basic components the apparatus figure 1 is used. In a clean flask it is added the required sunflower oil with 7% pentamaleinat quantity, tung oil and half colophon esterified with glycerin quantity according to the recipe (table 5). The mixture is stirred heating. When temperature reached 170°C after 5 minutes it is added the remained colophon esterified with glycerin quantity heating up to 190°C, than phenol formaldehyde resin and calcium rosinat is added. When the temperature reached 240°C yellow lead oxide is added in portions and the temperature is gradually increased to 285-290°C and is kept constant for 25 minutes. After this the mass is cooled up to 150°C when the white spirit is added. The whole process took 1h and 50 min. The mass viscosity resulted 4 sec. time in which 25ml white-spirit is added. After the dilution the viscosity was 3 sec. (with bubble method). The physico-chemical properties are given at table 6.

Table 6 - Physico-chemical properties of paint basic components

	Description of property	Unit	Paint basic components	Standard
1	Viscosity	seconds	3	2 - 3.2
2	Acid Value	mg KOH/g	3.73	≤ 10
3	Solid	%	68.8	70±2

B. The preparation of the grey anticorrosive paint. This process went through two phases, preparation of coloring paste according to the recipe shown at the table 7 and the preparation of the final product according to the recipe [1], [8], shown at the table 8.

Table 7 - Recipe of coloring paste grey

8	Row materials	%
1	Paint basic components	30.0%
2	ZnO	63.0%
3	$CaCO_3$	6.5%
4	Lampblack	0.5%

After the components given at table 7 are well mixed the homogenous mass is refined. The refinement went on until the fines reached 60µ.

Table 8 - Recipe of grey anticorrosive paint

	Row materials	%
1	Coloring paste	73.6%
2	Paint basic components	23.4%
3	Cobalt naphthenat (3%)	0.25%
4	Manganese naphthenat (3%)	0.67%
5	White-spirit	2.08%

The properties of grey paint formulated according to the recipe of tab.8 are summarized at table 9.

Table 9 - Physical properties of grey paint

	Description of physical property	Unit	Grey paint
1	Fines	µ	50
2	Drying time surface drying time full paint drying time	 hour hour	 2.5 23
3	Viscosity Ford cup B_4 25±1˚C	seconds	70
4	Coating capacity	g /m^2	60
5	Elacticity	mm	1
6	Shock endurance	cm / kg	50

C. The preparation of the brown anticorrosive paint. This process went through two phases, preparation of coloring paste according to the recipe shown at the table 10 and the preparation of the final product according to the recipe shown at the table 11.

Table 10 - Recipe of coloring paste brown

	Row materials	%
1	Paint basic components	25.5%
2	Sunflower oil with 7% pentamaleinat	2.9%
3	Fe_2O_3	28.6%
4	$CaCO_3$	43%

After the components given at table 10 are well mixed the homogenous mass is refined. The refinement went on until the fines reached 60µ.

Table 11 - Recipe of brown anticorrosive paint

	Row materials	%
1	Coloring paste	69%
2	Paint basic components	28%
3	Cobalt naphthenat (3%)	0.3%
4	Manganese naphthenat (3%)	0.4%
5	White-spirit	2.3%

The properties of brown paint formulated according to the recipe of tab.11 are summarized at table 12.

Table 12 - Physical properties of brown paint

Nr	Description of physical property	Unit	Brown paint
1	Fines	µ	60
2	Drying time surface drying time full paint drying time	 hour hour	 3.5 23
3	Viscosity Ford cup B_4 25±1˚C	seconds	80
4	Coating capacity	g /m^2	50
5	Elasticity	mm	1
6	Shock endurance	cm / kg	50

CONCLUSIONS

The intention of improving the physico-chemical properties of the semidrying oils through the thermo-chemical processing is theoretically and experimentally proved. After the transformation in pentholes containing pentamaleinates the semi drying oils become part of the dryable group of oils. The sunflower oil for example, obtains the properties of the linseed oil after the being processed with pentaerythritol through thermo-processing.

The optimal thermo-processing conditions are: The content of penthamaleinat 7%. The temperature of the alcoholysis 250°C. The processing time 30-50 minutes. The esterification temperature 240°C and the necessary time 2 hours. The polymerization temperature 290°C and the time interval 6-8 hours.

The physico-chemical as well as the technological properties of penthols with 7% penthamaleinat are the same as those belonging to the linseed oil.

The characteristics of grey and brown paints prepared with sunflower oil with 7% pentamaleinat are according to standards.

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