

## Preparation of the anticorrosive paints with long oil alkyd resins modified with maleic anhydride and phthalic anhydride

*Long oil modified alkyd resins have a wide usage as film forming substances with protection characteristics at anticorrosive paints.*

*Alkyd resins have replaced the basic components of the anticorrosive paints, which formerly were produced through thermo-chemical processing of colophon products with polymerized vegetable oils. Until the year 2000 the colophon half products used in our country have been calcium rosinat, lead rosinat, esterified colophon with glycerin or pentaerythritol, phenol formaldehyde-modified resin with colophon etc.*

*In the present paper we report the usage of maleic anhydride as a partial replacement of phthalic anhydride in long oil modified alkyd resins. The usages of maleic anhydride as a partial replacement of phthalic anhydride at these resins as well as at the vegetable oils improve the characteristics of the film of paint, such as its hardness and its resistance against atmospheric and corrosive agents. Maleic anhydride influences also in the condensation time of alkyd resins. Usually, the maleic anhydride is added before the phthalic anhydride, because it links with the double bonds of the radicals of vegetable oils, raising the stereo chemical structure and helps to achieve, in a short time, the proper viscosity of the resin. Experiments have shown that the optimal quantity of maleic anhydride for achieving the desirable results is 2%.*

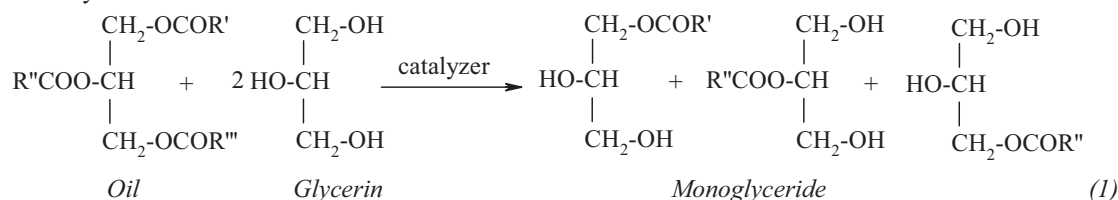
### INTRODUCTION

Anticorrosive paints like all other types of paints are dispersions consisting of two phases: 1. Liquid phase that is the solvent of the film forming substance with different organic solvents. 2. The solid phase formed from pigments and inert ingredients. The solvent of the film forming substances (paint basic components with modified alkyd resins) gives to the paint film stickiness to metal surfaces, resistance to the humidity and other atmospheric agents. The properties of the film are improved due to the inhibition effect of some pigments like  $\text{Fe}_2\text{O}_3$ ,  $\text{Pb}_3\text{O}_4$  etc [5],[6].

The alkyd resins modified with long oil used for anticorrosive paints in our country are manufactured with the alcoholysis method. Due to the shortage linseed oil and referred to the literature [4] the substitution of phthalic anhydride with maleic anhydride is experimented for the preparation of the alkyd resins with sunflower [2].

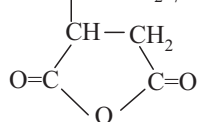
The main reactions that happened are:

#### a. Alcoholysis

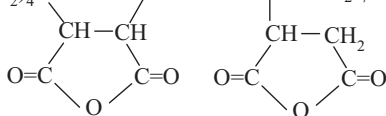
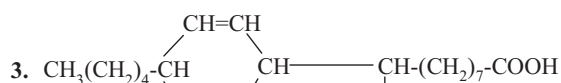


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b. The join addition of maleic anhydride happens to the double bond at the chain extremity. The products of the addition of one or two molecules of maleic anhydride with oils are presented with structures (2) and (3). Structure 3 presents a product according to Diels-Alder synthesis [10].

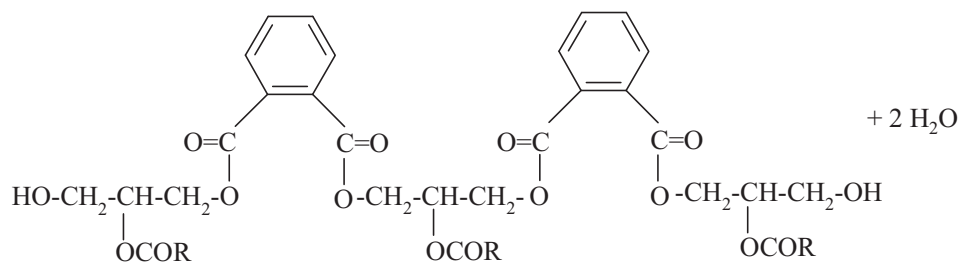
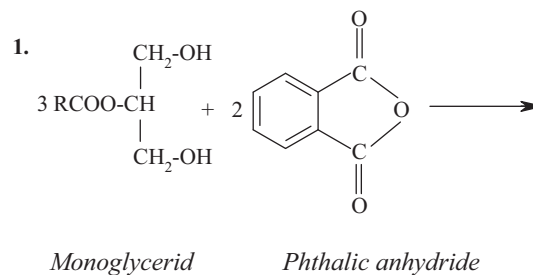


(2)

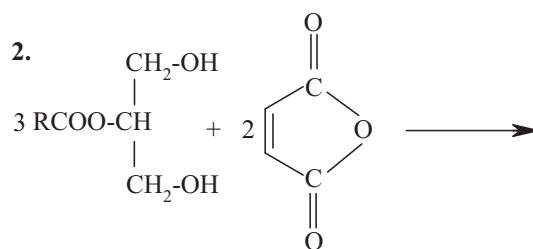
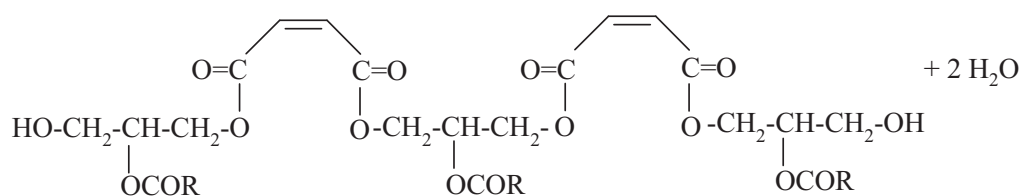


(3)

c. Esterification with phthalic anhydride and maleic anhydride (Azeotropic esterification) [9]



(4)

*Monoglycerid**Maleic anhydride**Maleic alkyd resin*

(5)

After the esterification the alkyd resin has a stereo structure and a tendency to become gelatinized and for that reason the use of maleic anhydride must not be exaggerated.

#### EXPERIMENTS AND RESULTS

To perform this experiment is used the apparatus of the figure 1.

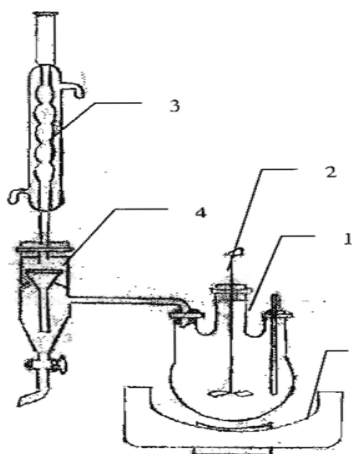


Figure 1 – 1 - Flask 3 neck, 2 – Stirrer, 3 – Condenser, 4 - Dropping funnel

There are prepared different resins formulations changing the ratio between maleic and phthalic anhydrides as well as the oil length [8]. Apart from the variations of the quantities of reaction components the experiment went as follows: In the flask

are added sunflower oil and glycerin. The temperature is raised to 120°C for 0.5 h and then PbO as catalyzer is added. The temperature is further raised for 1 h at 240°C until the alcoholysis is realized. It is considered finished when 1 ml of resin dilutes in 1ml methanol and the solution is clear. The mass is cooled to 210°C and then maleic anhydride and phthalic anhydride in portions (4-5) for 15-20 minutes are added. The dropping funnel is filled with 60 ml xylene and a quantity of refluxing xylene is added in the flask. The temperature is gradually raised up to 200-210°C and then the reaction born water is removed in portions (4 portions, every 15 minutes) [9]. The temperature is raised up to 240°C and meanwhile esterification and viscosity growth go on. The viscosity is monitored every 30 to 60 min. up to the permitted limits. Late the alkyd resin is cooled up to 150°C, is diluted with white spirit and after 20 min. of mixing the properties are determined. (Viscosity, acidity and solid).

The experiments concerning the use of maleic anhydride have begun with alkyd resins with 50% semi drying vegetable oils.

According to the data of the tables and graphics, results that the used maleic anhydride can't exceed the 2% of phthalic anhydride quantity.

The method used for the alkyd resin process is the alcoholysis method combined with azeotropic esterification with refluxing xylene which carries away the reaction water [9]. The applied recipes [8] are presented at the table 1.

Table 1 - Recipe of alkyd resins modified with oil 50%

	Row materials	Unit	I		II		III		IV	
1	Sunflower oil	%	26.1		26.1		26.1		26.1	
2	Glycerin	%	8.2		8.2		8.2		8.2	
3	Phthalic anhydride	%	17.3	100	17.1	99	16.95	98	16.4	95
4	Maleic anhydride	%	-	0	0.2	1	0.35	2	0.9	5
5	PbO	mg	5.7		5.7		5.7		5.7	
6	Refluxing xylene (1)	%	1.8		1.8		1.8		1.8	
7	Funnel xylene (2)	%	60		60		60		60	
8	White spirit	%	46.6		46.6		46.6		46.6	

Note:

1. In reckoning up the resin percentage, xylene 1 and white spirit as a solvent are included.
2. The quantity of the maleic anhydride is reckoned up as a percentage of the maleic anhydride quantity.

The phases of the preparation of the modified alkyd resin with maleic and phthalic anhydrides are relised according to the table 2.

Table 2 - Phases of preparation of alkyd resin

	The phases of the preparation of resin	Unit	Experimented resins			
			I	II	III	IV
1	Reaction time to 120°C	min.	34	30	30	30
2	Reaction time to 240°C	min.	60	60	60	60
3	Alcoholysis time	min.	60	60	60	60
4	Reaction and water removal time	min.	185	120	120	120
5	Esterification and polycondensation time	min.	160	200	175	20

Note: The alcoholysis is considered finished when the solubility of 1 part of resin with 5 parts of CH<sub>3</sub>OH forms a clear solution. The physico-chemical properties after the dilution with white spirit 1:1 are presented at the table 3.

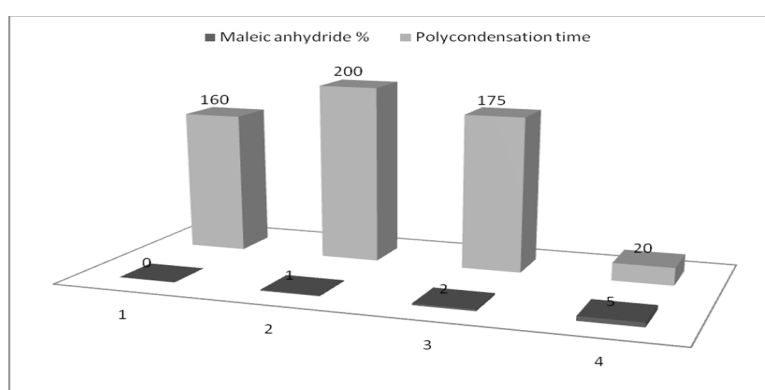


Figure 2 - Change of the polycondensation time from maleic anhydride percentage

As it shows fig. 2, the polycondensation time concerning the resin IV with 5% maleic anhydride is 20 min. This means  $\approx 12\%$  of the polycondensation time of the resin III with 2 % maleic anhydride.

Table 3 - Physico-chemical properties of alkyd resins

	Description of property	Unit	I	II	III	IV
1	Acid Value	mg KOH/g	7.3	8.36	9.1	9.6
2	Viscosity (bubble method)	seconds	6.4	6.5	6.9	7.9
3	Solid	%	50.1	48.8	48	49.6
4	Colour (CoCl <sub>2</sub> + FeCl <sub>3</sub> )		8	7	6.5	6.5

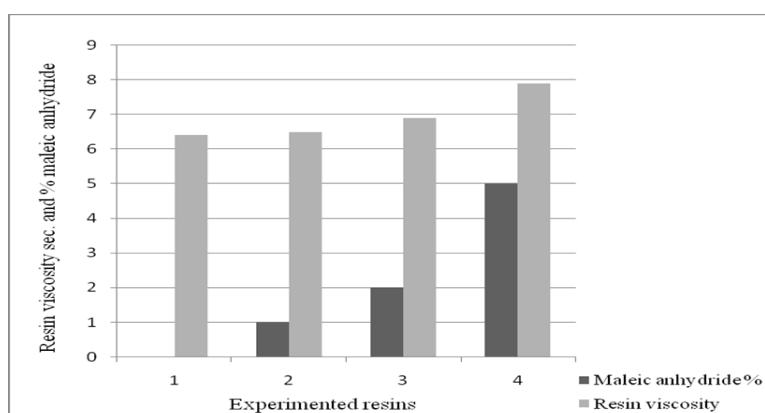


Figure 3 - Change of the viscosity from maleic anhydride percentage of alkyd resins modified with oil 50%

The experiments are repeated with long oil resin  $\approx 60\%$  proceeding with same procedure. The used recipes are shown at the table 4, choosing only the recipes for resins I, III and IV from table 2.

Table 4 - Recipe of alkyd resins modified with oil 60%

		Unit	I		II		III	
1	Sunflower oil	%	34.4		34.4		34.4	
2	Glycerin	%	8.2		8.2		8.2	
3	Phthalic anhydride	%	16.7	100	16.37	98	15.86	95
4	Maleic anhydride	%	-	-	0.33	2	0.84	5
5	Refluxing xylene (1)	%	4.5		4.5		4.5	
6	Funnel xylene (2)	%	60		60		60	
7	PbO	mg	10		10		10	
8	White spirit	%	36.2		36.2		36.2	

Note:

1. For the calculations, the refluxing xylene is also taking into account supposing it remains at the mass.

2. The calculation for the length of the oil is made after this formula:  $(L+A+B) - (9A/74) = 100$

Where:

L- Oil mass

A - Maleic anhydride mass

B - Glycerin mass

9A/74 - Water reaction mass

The physico-chemical properties after the dilution with white spirit 1:1 are presented at the table 5.

Table 5 - Physico-chemical properties of alkyd resins

	Description of property	Unit	I	II	III
1	Acid Value	mg KOH/g	10.07	10.39	9.87
2	Viscosity (bubble method)	seconds	8	9.3	12
3	Solid	%	63	63.8	60.5
4	Colour (CoCl <sub>2</sub> + FeCl <sub>3</sub> )		9	8.5	7.5

In conformity with the properties the best alkyd resin to be used for anticorrosive paints is resin II. In order to avoid the viscosity control of the alkyd resin, no experiment is performed with more than 5% maleic anhydride instead of phthalic anhydride.

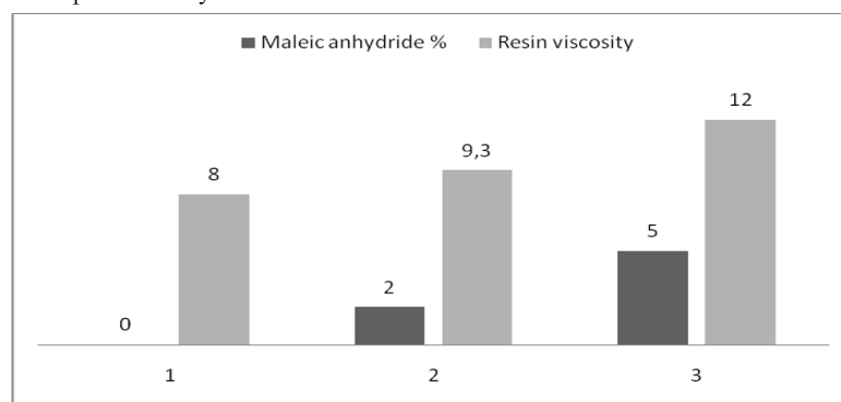


Figure 4 - Change of the viscosity from maleic anhydride percentage of alkyd resins modified with oil 60%

As it shows fig. 4 and table 5, for the resin III with 5% maleic anhydride the viscosity is too high although the solid percentage is low. The viscosity raises as the result of the polymerization degree.

Table 6 - Recipe of coloring paste

	Recipe of coloring paste preparation	%
1	Long oil alkyd resins (Resin II)	41.8 %
2	Red iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	22 %
3	ZnO	1 %
4	Pb <sub>3</sub> O <sub>4</sub>	5.5 %
5	BaSO <sub>4</sub>	11 %
6	Aluminium stearate 6%	0.37 %
7	Cobalt naphthenat (3%)	8.33 %

#### The preparation of the anticorrosive paint.

This process went through two phases, preparation of coloring paste according to the recipe shown at the table 6 and the preparation of the final product according to the recipe shown at the table 8. The

recipe is taken from the experience of anticorrosive paint preparation at Tirana paint factory [8]. The paint basic components at recipe of coloring paste (table 6) it is replaced with resin II (according table 4).

After the components of coloring paste, given at table 7 are well mixed the homogenous mass is refined. The refinement went on until the fines reached 60 $\mu$ .

Table 7 - Recipe of anticorrosive paint

	Recipe of anticorrosive paint preparation	%
1	Coloring paste (Table 6)	95 %
2	Cobalt naphthenat (3%)	0.7 %
3	Manganese naphthenat (3%)	0.7 %
4	Lead naphthenat (12%)	1 %
5	White spirit (added till $\eta$ is...)	$\eta = 70 - 120$ secs with Ford cup B <sub>4</sub> 25 $\pm$ 1 $^{\circ}$ C

The physical properties of anticorrosive paints are presented at the table 8.

Table 8 - Physical properties of anticorrosive paints and the comparison with standards [7]

III	Description of physical property	Unit	Anticorrosive paint prepared with resin II with long oil	Anticorrosive paint prepared with colophon products	Standard
1	Viscosity Ford cup B <sub>4</sub> 25 $\pm$ 1 $^{\circ}$ C	seconds	105	90	70-120
2	Fines	$\mu$	60	60	60
3	Drying time				
	surface drying time	hour	0.75	4	8
	full paint drying time	hour	5	8	24
4	Coating capacity	g/m <sup>2</sup>	60	60	60
5	Shock endurance	cm/kg	50	50	50
6	Elasticity	mm	1	1	1
7	Endurance of paint in salt water		e mirë	e mirë	e mirë
8	Stickness ( $\varnothing$ 5mm) (method with concentric circles)		1-2	1-2	1-2

#### DISCUSSIONS AND CONCLUSIONS

- The use of maleic anhydride as partial replacement of the phthalic anhydride was theoretically supported and practically confirmed.

- Maleic anhydride makes the stereo structure of the alkyd molecule bigger although the used oils are part of the oil group called semi drying with 4-6

conjugated double bonds. As shown at the related tables maleic anhydride gives:

- Reduction of the polycondensation time.
- The viscosity increases from 6.4-6.5 seconds to 7.9 secs. within the same time interval.
- The colour decreases from 8 to 6.5 and this due to the fact that during the polymerization the time

becomes shorter and as the result also the contact with the oxygen.

- Resin with long oil replaces completely the anticorrosive paint base thus ensuring the physico-chemical properties of the film after drying.

- The use of maleic anhydride up to 2 % instead of phthalic anhydride gives better results.

- When maleic anhydride is used up to 5% instead of phthalic anhydride the resin tends to become gelatinized during the process of polymerization making very difficult the viscosity control.

- In coating systems alkyd resins still play an important role because of their benefits such as the economical balance, an uncomplicated application and an outstanding appearance of the films.

- The characteristics of anticorrosive paint prepared with alkyd resin modified with 2% maleic anhydride are according to standards.

#### REFERENCES

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