NEW SYNTHETIC VARNISHES FROM LOCAL COAL-TAR PHENOLS

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SUMMARY: Locally producer coal-tar phenols were fractionally distilled and the required fraction which rich with phenol was collected and specified. This phenolic fraction was methylated and acylated with selected acid chlorides to the corresponding ketones which then reduced and finally demethylated to the required alkyl phenols. These alkyl phenols were condensed with formalin to produce the corresponding alkyl phenol-formaldehyde resin which the processed to the required varnishes. Several formulations from the prepared varnish samples were chosen and their electrical and chemical properties were examined.

Key Words: Insulating varnishes, coal-tar phenols.

INTRODUCTION

A good insulating varnish is of prime importance in the construction of electrical equipment. The life and performance of which depends to a great extent of the total insulation.

Insulation varnishes may be divided into three groups (1): a. Baking type insulating varnishes, b. Air-drying insulating varnishes, and c. Other types of insulating varnishes.

The development of new resins such as alkyed (13) and oleo resinous varnishes (3), hydrocarbon resins (9), phenolics (17), Vinyls (10), and epoxy (8,11) silicon and polyurethane (18), had provided the varnish manufacture with great incentive to improvement, and although it takes a long time to evaluate fully and safely new insulating varnishes.

Synthetic resin chemistry is advancing so rapidly that oil modified synthetic varnishes are expected to be used for a long time in the future.

MATERIALS AND METHODS

The starting materials used were

a. Coal-tar phenols as a product of El-Nasr Co for Coke and Basic chemicals (EL-Tabbin, Helwan, Egypt) which have the following specifications: boiling range 170-225°C, Sp. gr. at 15/4°C= l.0143, n_D^{25} = 1.5551, and average molecular weight 101.

b. Toluene diisocyanate (TDI) which is mainly mixture of 80% 2,4- and 20% 2,6-toluene diisocyanate.

Purification and distillation of coal-tar phenols

The locally produced coal-tar phenols were firstly dried by anhydrous magnesium sulphate and then fractionally distilled. The required fraction rich with phenol was collected and specified, Table 1.

Preparation of fatty acid chlorides

Three acid chloride of long chain fatty acids, namely, lauric, palmitic, and stearic acids were prepared by using thionyloride as given in (12).

Preparation of alkyl phenols

The phenolic fraction was firstly methylated as described in (15) and termed as (A), then acylated with the prepared acid chlorides following a procedure as described in (6,15) to produce the corresponding ketones which termed as (A_1, A_2, and A_3). These ketones were reduced by Clemmsen's reduction method (7) to produce a products which termed (B_1, B_2, and B_3). The required alkyl phenols were obtained by the usual demethylation procedure and termed as (C_1,C_2, and C_3). Table 2 shows the specifications of the obtained products A, A_1-A_3, B-B_3, and C_1-C_3, respectively.

Preparation of alkyl phenols-formaldehyde resins

Many attempts were made to convert each of these alkyl phenols substances into alkyl phenol-formaldehyde resins under different conditions (Concentration, temperature contact

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Table 1: Specifications of the phenolic fraction.

	Boiling range (°C)	sp.gr.at 15/4 (°C)	n_D^{25}	Average M. wt	Yield % (based on the unpurified coal-tar phenols)
Phenolic fraction	175-185	1.0345	1.5439	95	40

time, and catalyst. The following technique was followed, and the formulation was given in Table 3. A solution of alkyl phenols products in toluene, formalin (40%), and hydrochloric acid (33%) as a catalyst, were slowly heated to 95°C while the exothermic reaction progressed. After 90 minutes refluxing at 95°C, the amount of water formed was removed. After cooling to 5°C, the resins was washed with water, then the toluene was distilled off to obtain the required resins (F, F_1, F_2, and F_3)

The specification of alkyl phenol-formaldehyde resins were shown in Table 4.

Formulation of the varnishes

In the present work, several formulations were tried to obtain varnish samples. The best samples were obtained by mixing the components in the proportions, shown in Table 5.

The general procedure for formulation was as follows:

Toluene diisocyanate 87 g and toluene xylene mixture (1:1) 87 g were heated to 115°C during 30 minutes. Then the alkyl phenol- formaldehyde resins (Table 3) was mixed with the resulting mixture under reflux, followed by addition of triethylamine as a catalyst (6% based on the alkyl phenol-formaldehyde resin) for 1.5 hours at 130-140°C to give the required varnish samples, which termed as V, V_1,V_2 and V_3.

Evaluation of the prepared varnishes

Samples (alkyl phenol-formaldehyde-diisocyanate) were screened as electrical insulating varnishes according to Standard methods (16). Aguarde-ring capacitor type NFM/ST was used dielectric constant and power factor were measured at 60 cycles. The accuracy of the measurements of dielectric constant was 1%, while for power factor was #2%. Description of the instrument and methods used for measurements and calculations were also given in (16). Measurements were carried out at temperature 30°C. Loss factor is the product of the dielectric constant and the power factor and is a measure of total losses in the dielectric material. The results were given in Table 6 and represented in Figure 1.

DISCUSSION

Phenol-formaldehyde resin (Novolak) was reacted with isocyanates to from Novolak isocyanate synthetic resin. In the present work alkyl phenols (where alkyl = lauryl of palmityl or stearyl) were prepared, then reacts with formalin giving alkyl phenol-formaldehyde resins, which reacted with toluene diisocyanate to from alkyl phenol-formaldehyde-diisocyanate synthetic varnishes.

The fundamental properties of insulating varnishes are as follows,

1. Electrical properties (dielectric constant, power factor, and loss factor),

2. Chemical properties (water and chemicals resistance, through drying and cure in depth).

The data obtained in Table 6 show that the dielectric constant of the sample V_3 (formulated from stearyl phenol-formaldehyde resin) is 3, of the sample V_2 (formulated from palmityl phenol-formaldehyde resin) is 3.5, of the sample V_1 (formulated from lauryl phenol-formaldehyde resin) is 4.1, and of the sample V (formulated from phenol-formaldehyde resin) is 4.5. This means that the dielectric constant of these samples is in the order $V_3>V_2>V_1>V$ since V_3 has the lowest value of dielectric constant.

At the same time, the power factor of the sample V_3 is 0.0026, of the sample V_2 is 0.0028, of the sample V_1 is 0.0036, and of the sample V is 0.0046. This means that the power factor, of these samples in the order $V_3>V_2>V_1>V$ since V_3 has the lowest value of power factor.

Table 2: Specifications of methylated phenolic fraction, prepared ketones, methylated alkyl phenols and alkyl phenols.

Compound Specification	A	A1 Lauryl	A2 Palmityl	A3 Stearyl	B1 Lauryl	B2 Palmityl	B3 Stearyl	C1 Lauryl	C2 Palmityl	C3 Stearyl
Yield % (based on the unpurified coal-tar phenols)	79	72.1	79.5	80	37.2	80.5	82	43	47	45
Average M. wt.	107	289	345	373	275	331.5	360	261	312	346
C %	77.6	80	80.2	82.9	82.9	83.3	83.3	82.7	83.2	83.2
H %	7.4	10.3	11	11.2	11.6	12	12.2	11.5	11.9	12.1

Table 3: Formulation of alkyl phenol-formaldehyde resins.

Sample parts by wt., gm	F	F_1	F_2	F_3
Phenol	20	-	-	-
Lauryl phenol	-	15	-	-
Palmityl phenol	-	-	40	-
Stearyl phenol	-	-	-	33
Formalin	9	6.5	18	14
Hydrochloric acid	1.25	1	2.5	2.1

It is clear from Table 6 and Figure 1 that the loss factor of the sample V_3 is 0.0078, of the sample V_2 is 0.0098, of the sample V_1 is 0.0147 and of the sample V is 0.0207. This means that the loss factor of these samples is in the order $V_3>V_2>V_1>V$ since V_3 has the lowest value of loss factor.

This also indicates that the electrical properties (dielectric constant, power factor, and loss factor) of the sample V_3 is superior than that of the other samples, which may be due to the presence of stearyl group -the longest alkyl group- in the structure of this sample (stearyl phenol-formaldehyde-diisocyanate varnish) i.e. this is valuable intermediates in the synthesis of alkyl phenol-formaldehyde-diisocyanate varnish.

This proves that the electrical insulation properties improves gradually with increasing the number of (-CH_2-) units in the alkyl group of (0 to 18 carbon atoms) present in the samples.

On the other hand, the sample V has the highest dielectric constant, power factor, and loss factor value. This may be due to the absence of alkyl group in the formulation of this sample.

A good insulating varnish has a low dielectric constant, low power factor, and low loss factor properties. This phenomenon is attributed to the orientation motion of individual segments (units) or components parts of each resin (polymer) chain depends on conformational changes and thermal motions. Hence, the ability of the polymer groups to switch orientation in phase with an alternating current may be limited. This phase lag results in an absorption of energy through this resin (polymer) (2, 5,14). This shows that samples V that has a high dielectric constants, high power factor, and high loss factor absorbs a considerable amount of heat from the alternating electrical field. Hence, such samples (varnishes) may soften or melt and lose their insulation capability.

Sample V_3 has a low dielectric constant, low power factor, and low loss factor, and thus is suitable for using as an electrical insulator, due to, the ability of the stearyl group to switch orientation in phase with an alternating current may be limited. This phase lag results in an absorption of energy through this sample. Also, we can observe from Table 6 that the water absorption of the sample V_3 is 0.054 %, better than sample V_2 0.058%, better than sample V_1 0.105%, and also better than sample V 0.0151%. This indicates that the water absorption of sample V_3 has the lowest value.

Table 4: Specifications of the alkyl phenol-formaldehyde resins.

Sample Characteristics	F	F_1	F_2	F_3
Specific gravity at 20°C	1.26	1.40	1.48	1.52
n_D^{25}	1.4880	-	-	-
Softening point, °C water absorption, %	62	69	75	77
24 hours at 25°C	1.76	1.80	1.79	1.82

Table 5: Formulations of the varnishes.

Samples Parts by wt., gm	V	V_1	V_2	V_3
Phenol-formaldehyde	25	-	-	-
Lauryl phenol-formaldehyde	-	15	-	-
Palmityl phenol-formaldehyde	-	-	38	-
Stearyl phenol-formaldehyde	-	-	-	35.5
Toluene diisocyanate (dissolved in toluene-xylene)	30	18	45.6	42.7
Triethylamine	1.5	0.45	2.2	1.8

CONCLUSIONS

From the data obtained the following conclusions could be observed,

1. The electrical insulation properties of the prepared samples were found to be: Stearyl phenol-formaldehyde-diisocyanate>palmityl phenol-formaldehyde-diisocyanate>lauryl phenol-formaldehyde - diisocyanate samples.

2. The electrical insulation of the prepared samples is improved by increasing the number of -CH_2-Units in the alkyl group of (0 to 18 carbon atoms) present in the samples.

Table 6: Properties of the varnishes.

Sample Specifications	V	V_1	V_2	V_3
Dielectric constant, (60 cycles)*	4.5	4.1	3.5	3
Power factor, (60 cycles)*	0.0046	0.0036	0.0028	0.0026
Loss factor*	0.0207	0.0147	0.0098	0.0078
Water absorbtion, 24 hours immersion, weight change, %**	0.151	0.105	0.058	0.054
Time of drying, hr	8	6-8	4-5	3
Colour, Appearance	Reddish Browth Opaque			
	Solution viscous		Semi-solid	

* ASTM D-150, ** ASTM D-570

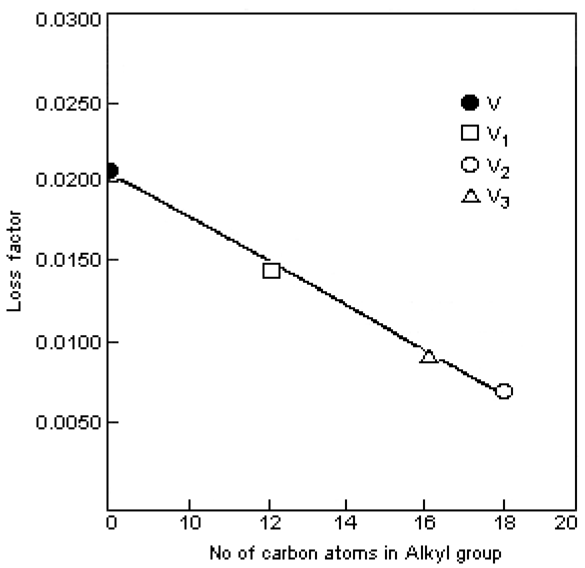

Figure 1: Loss factor versus number of carbon atoms for prepared alkyl phenol-formaldehyde disocyanate varnishes.

3. The insulating varnish sample (stearyl phenol-formaldehyde-diisocyanate) proved advantageous to the order samples because of, a) having low dielectric constant, low power factor, low loss factor and low water absorption, b) the presence of stearyl group having an alkyl group of 18 carbon atoms in the formulations of this sample. Hence the ability of the alkyl to switch orientation in phase with an alternating current may be limited. This phase lag results in an absorption of energy through this alkyl group.

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