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Preparation and evaluation of the antibacterial alkyd resin modified with 2,2\ -di-thiosalicylic acid

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ABSTRACT

This paper reported on the synthesis of a series of modified alkyd resins by partial replacement of phthalic anhydride with 2,2\-di-thiosalicylic acid. The modifier containing aromatic ring and sulphur atom which enhancing the physical, mechanical and chemical properties of the modified alkyds, especially at higher content. The antibacterial activitywas also investigated and gave promising results which promoted the application of the modified alkyds and in antibacterial aspects especially at high modifier content.

KEYWORDS

Alkyd resin;
2,2\ -Di-thiosalicylic acid;
Antibacterial activity;
Chemical resistances;
Mechanical properties.

INTRODUCTION

Since 1930s, Alkyd resins have been used as a major binder for paints. Their compatibility with many polymers and the extremely wide formulating latitude made them suitable for the production of a very broad range of coatingmaterials[1]. This includes do-it-yourself paints and varnishes for wood and metal, road marking paints, etc. Also, due to the wide use of coatings in different fields such as the automotive, shipbuilding and textile industries, it is important for companies to develop new coating materials havingperformance propertiessuch as hardness, flexibility, abrasion resistance, chemical resistance,anticorrosive and antibacterial activity[2].

The coatings propertiesare basically depend on the resin which is used in its formulation, therefore, the alkyd resin plays a very important role in the coating formulation[3]. Alkyd resins are the reaction products of polybasic acids, polyhydric alcohols and monobasic fatty acids or oils. It is a chemical combination between oil or oil-derived fatty acids and polyester polymer, thus enhancing the mechanical properties, drying speed durability of these oleoresinous vehicles formed over and above those compared with the oil themselves[4].

It is possible to produce alkyds with greatly improved resistance to hydrolysis by the use of acid containing sterically hindered carboxyl groups, such as the “versatic acids”. These are a mixture of heavily branched aliphatic acids with 9 to 11 carbon atoms and with most (> 93%) of carboxylic groups attached to a quaternary carbonation. Oil modified alkyd resins are made with drying semidrying and non-drying oils. The type of oil selected depends on the conditions under which the film will be dried and the color retention properties required in the film. Air drying alkyds are made with the good drying oils such as linseed oil and dehydrated castor oil, but semidrying soya bean oil may also be used in medium and short–oil alkyds. In general, soyabean oil–modified alkyds are not satisfactory for air –drying varnishes[5].

Various vegetable oil sources that are used for alkyd preparation include tall oil, soya oil and many others; acommon property of these oils is their high degree of unsaturation. Also, examples of polyhydric alcohols are glycerol, ethylene glycol, pentaerythritol and trimethylolpropane while the commonly used acids/anhydrides are phthalic anhydride, isophthalic anhydride and maleic anhydride[6]. The oil chosen for the production of alkyds usually has a profound effect on the properties of the finished alkyds, and they are used in an air-drying water-reducible lacquer formulation[7].

Modified alkyd resin lacquers were prepared from Soya oil, pentaerythritol, phthalic anhydride and Dacron by mixing with pigments, talc and a diluent and a drying agent, milled and filtered to form modified alkyd resin–based paints[8-9].

In this research work modified alkyd resin was prepared by partial replacement of phthalic anhydrideby 2,2'-di-thiosalicylic acid. The chemical, mechanical, stoved and air dry film properties due to the partial replacement of the acid have been evaluated. Also, the biological activity of the resins in addition to their varnishes wereinvestigated.

EXPERIMENTAL

Materials

Linseed oil fatty acidwas supplied by Echantillon, Belgium. Phthalic Anhydride and Glycerol were obtained from El-Nasr Pharmaceutical Chemical Company, Egypt. Diethanolamine and 2,2\ -Di-thiosalicylic acid were obtained from Merck Germany.

Synthesis of modified alkyd resins

The preparation of various modified alkyd resins based on linseed oil fatty acid was carried out via solvent process in one-step reaction as follows: The calculated amounts ofanhydrous glycerol as the ingredient source of the polyol, linseed oil fatty acid and phthalic anhydridereplaced partially with2,2\ -Di-thiosalicylic acid as the ingredient source of the polybasic acids, were mixed in 250 ml round-bottomed flask fitted with Dean and Stark apparatus and refluxed in the presence of 10 % xylene. The course of the esterification was followed by observing the theoretical amount of water liberated. The resins were prepared, covering a wide range of oil lengths and hydroxyl contents (0, 10, 20, and 30 % Excess–OH). It should be note that within each set of formulations the total number of acid and hydroxyl equivalent for the various runs were kept constant[10]. Resin characteristic constant and weight changes of the various formulations are illustrated in TABLES 1-2. Alkyd calculations can be used to pre-

TABLE 1: Resin contents for DTSA modified polyester

Resin No.	Excess –OH %	Ingredients	E	F	e_0	e_A	e_B	R	K	H_2O off (ml)
I_{a-d}	0	G	30.7	3	0.520	0.260	0.260	1.00	1.05	3.34
		DTSA	153	2						3.48
		LOFA	280	1						3.61
		PA	74.1	2						3.75
II_{a-d}	10	G	30.7	3	0.573	0.273	0.300	1.10	1.05	3.36
		DTSA	153	2						3.51
		LOFA	280	1						3.67
		PA	74.1	2						3.83
III_{a-d}	20	G	30.7	3	0.656	0.298	0.358	1.20	1.04	3.42
		DTSA	153	2						3.63
		LOFA	280	1						3.81
		PA	74.1	2						4.01
IV_{a-d}	30	G	30.7	3	0.778	0.339	0.439	1.30	1.01	3.55
		DTSA	153	2						3.79
		LOFA	280	1						4.06
		PA	74.1	2						4.31

G: Glycerol,DTSA: 2,2\ -Di-thiosalicylic acid,LOFA: Linseed oil fatty acid, PA: Phthalic anhydride, E: Equivalent weight, F: Functionality,e_o: Total equivalent present at the start of the reaction,e_A: Number of acid equivalent, e_B: Number of hydroxyl equivalent, R: Ratio of total–OH groups to total–COOH groups (e_B/ e_A), K: Alkyl constant (m_o/e_A),m_o: Total moles present at the start of the reaction

TABLE 2 : List of acid equivalent of different runs

Resin	PA	DTSA
A	1.00	0.00
B	0.90	0.10
C	0.80	0.20
D	0.70	0.30

dict the completed formulation, properties of the resin, the amount of reaction water liberated and the probable risk of gelation. The calculation of water evolved is also useful both as a tool for following the course of esterification reaction and to find the theoretical yield.

Preparation of test panels

Glass and mild steel plates (50 x 150 mm) were degreased by dipping into petroleum ether, then the surfaces werecleaned by fine cloth, washed and wiped. The plates were washed with ethyl alcohol and allowed to dry in air. Films were applied onto clean plates and left for half an hour to remove slowly the greatest part of the solvent and then stoved at the required temperature for the specified time in a thermostatically controlled well–ventilated oven[11].

Physical and mechanical tests of films

A variety of physical, chemicals and mechanical evaluations of different alkyd resins were carried out according to American Society for testing materials (ASTM) include: Color (ASTM, D1544-98), Viscosity (ASTM, D1545-98), Non-volatile (N V) content (ASTM, D1644-1993), Drying time (ASTM, D 1640-95), Adhesion (ASTM, D3359-95), Flexibility (ASTM, D522-93), Gloss (ASTM, D523-89), Hardness (ASTM, D4366-95), Water resistance(ASTM, D870), Alkali resistance (ASTM, D1647-89), Acid resistance (ASTM, D3260-82) and Solvent resistance (ASTM Method, D2792-69).

Antibacterial activity

The antibacterial activity of the different modified resins against different kinds of bacteriawasestablished according toASTM D5589-97. Firstly, drawdown strips of different films were cut into a circle with 20 mm. these strips were placed at the center of solidified agar plates. Apply a thin coat of algae suspension to each specimen,making sure the surface is covered, but not oversaturating the samples. Transfer the inoculated plates to an incubator with a constant fluorescent light source, humidity ≥ 85 %, and a temperature setting to maintain 25 ± 2°C. The incubated samples were examined weekly for growth.

RESULTS AND DISCUSSION

During the course of esterification a newly modified antibacterial alkyd resins were obtained by partial replacement of phthalic anhydridewith2,2\ -di-thiosalicylic acid as the ingredient source of the polybasic acid. The reaction time was taken as the time required for collecting the theoretical amount of water at the trap. The effect of 2,2\ -di-thiosalicylic acid content and the excess hydroxyl groups on the reaction time was represented in Figure 1. From this Figure, it can be clearly shown that the reaction time increase by increasing both of the amount of 2,2\ -di-thiosalicylic acid added and excess hydroxyl group.

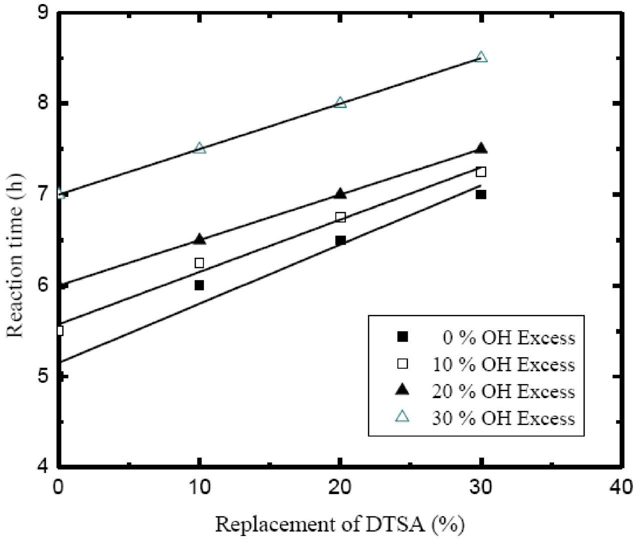

Figure 1: Reaction time as a function of 2,2\ -di-thiosalicylic acid and the excess hydroxyl groups contents

The effect of 2,2\ -di-thiosalicylic acid content on the physical properties of the modified alkyd resins are given in TABLE 3. According to these data, we can conclude that the color of the resins observed to be dark brown due to this partial replacement. The viscosity of the resins increased as the 2,2\ -di-thiosalicylic acid and/or hydroxyl group content had increased which is confirmed by the amount of non-volatile materials. Also, the drying time is observed to be proportional

TABLE 3 : Varnishes characteristics data

Resin No.	Excess-OH (%)	Replacement (%) of DTSA	Viscosity (gardner)	N V (%)	Color (Gardner)	Air drying time (h)	Stove			
							110 °C		120 °C	
							1h	2h	1h	2h
I$_a$	0	0	I	75	8	6.0	T	ST	VST	HD
I$_b$		10	K	78	>18	5.0	ST	ST	VST	HD
I$_c$		20	M	80	>18	4.0	ST	VST	VST	HD
I$_d$		30	Q	82	>18	3.0	VST	VST	HD	HD
II$_a$	10	0	K	76	9	6.0	T	ST	VST	HD
II$_b$		10	L	80	>18	4.5	ST	VST	HD	HD
II$_c$		20	Q	82	>18	3.5	VST	VST	HD	HD
II$_d$		30	S-T	83	>18	3.0	VST	HD	HD	HD
III$_a$	20	0	M	78	10	5.0	ST	ST	HD	HD
III$_b$		10	P	81	>18	4.0	ST	VST	HD	HD
III$_c$		20	R-S	83	>18	3.5	VST	HD	HD	HD
III$_d$		30	V-W	84	>18	2.0	HD	HD	HD	HD
IV$_a$	30	0	N	80	11	4.0	ST	VST	HD	HD
IV$_b$		10	Q	82	>18	3.0	VST	HD	HD	HD
IV$_c$		20	U-V	83	>18	2.5	VST	HD	HD	HD
IV$_d$		30	Z$_2$-Z$_3$	85	>18	2.0	HD	HD	HD	HD

with both 2,2\-Di-thiosalicylic acid and hydroxyl group contents which is confirmed by stoving.

TABLE 4 gives the mechanical properties of the various modified resins. These results indicate that the modified films show outstanding performance compared to unmodified films. The gloss results for the resins increases through the modification process which can be attributed to the incorporation of trihydroxylpolyol con-

TABLE 4 : Effect of DTSA on the mechanical properties of modified alkyd resin

Resin No.	Gloss at 20°		Flexability		Hardness (s)		Adhesion	
	A	s	a	s	a	s	a	s
I$_a$	90	92	Pass	Pass	61	62	5B	5B
I$_b$	92	93	Pass	Pass	62	63	5B	5B
I$_c$	92	94	Pass	Pass	62	64	5B	5B
I$_d$	93	95	pass	pass	63	65	5B	5B
II$_a$	91	93	Pass	Pass	61	62	5B	5B
II$_b$	93	94	Pass	Pass	63	64	5B	5B
II$_c$	95	95	Pass	Pass	64	66	5B	5B
II$_d$	95	96	pass	pass	65	68	5B	5B
III$_a$	92	93	Pass	Pass	63	64	5B	5B
III$_b$	94	94	Pass	Pass	64	67	5B	5B
III$_c$	95	96	Pass	Pass	65	67	5B	5B
III$_d$	96	97	pass	pass	67	68	5B	5B
IV$_a$	94	94	Pass	Pass	64	66	5B	5B
IV$_b$	95	94	Pass	Pass	65	68	5B	5B
IV$_c$	95	96	Pass	Pass	67	68	5B	5B
IV$_d$	96	97	pass	pass	68	69	5B	5B

a: air-drying films, s: stoved films

TABLE 5 : Effect of DTSA on the chemical properties of modified alkyd resin

Resin No.	Water resistance		Acid resistance		Alkali resistance		Solvent resistance	
	A	s	a	s	a	s	a	s
I$_a$	Ex	Ex	P	F	P	F	Ex	Ex
I$_b$	Ex	Ex	F	G	F	F	Ex	Ex
I$_c$	Ex	Ex	G	Ex	G	G	Ex	Ex
I$_d$	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
II$_a$	Ex	Ex	F	F	P	F	Ex	Ex
II$_b$	Ex	Ex	G	G	G	G	Ex	Ex
II$_c$	Ex	Ex	G	G	Ex	Ex	Ex	Ex
II$_d$	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
III$_a$	Ex	Ex	F	F	P	F	Ex	Ex
III$_b$	Ex	Ex	G	G	G	Ex	Ex	Ex
III$_c$	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
III$_d$	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
IV$_a$	Ex	Ex	F	F	G	G	Ex	Ex
IV$_b$	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
IV$_c$	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
IV$_d$	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex

P: Poor, F: Fair, G: Good, Ex: Excellent

taining a 2,2\-di-thiosalicylic acid rings within the resin structure. The presence of the repeating ester unit (–COOR) in the polymeric chain of alkyd resin improves its applications, as well as, enhancing the hardness property. The flexibility test for the different films were, carried out by the conical mandrel bending tester, show no evidence of cracks or de-laminating. This high flexibility is attributed to the polyester backbone. The cross-hatch test was carried out to determine the adhesion of the coating films, indicates clearly that, the modified coating has very good adhesion properties. This is indicate the ability of these modified resins for coating the pre-treated mild steel substrate is a good for preventing water ingress.

The chemical resistances of the new modified alkyd resins were undertaken on glass panels (25×75 mm). The resin coated glass panels were sealed using paraffin wax on the edges of the panels. The samples were immersed to half their length in the various test solutions (water, 5% by weight sodium hydroxide, 20% by weight sulphuric acid, and benzene / mineral turpentine solvent mixture 1 : 3 by volume). The panels were then removed from the solution, wiped carefully and allowed to dry at room temperature,thenthe immersed portion of the films were examined for any defects. The data tabulated in TABLE5 indicate that 2,2\-di-thiosalicylic acid content and the excess hydroxyl groups improve the film resistance towards acid and alkali and this improvement increases as these contents increased. However, this improvementdoes not appear towards water and solvent resistance properties.

The newly synthesized alkyd resins were tested for their antibacterial activity agents six types of bacteria including Bacillus subtils (ATCC 7972), Staphylococcus Aureus(NCTC 7447), Ascherichi Coli (NCTC 10416), Pseudomonaaeruginosa(ATCC 10145), Candida Albicans(IMRU 3669), and Aspergillus Niger (ATCC 6275),usingASTM D5589-97. According to this method the evaluation process depends on noticing the microbialgrowth rateon the specimen weekly for three weeks. The zero rating means no microbial growth on the specimen while 1, 2, 3, and 4 ratings means traces of growth (<10 %), light growth (10-30 %), moderate growth (30-60 %), and heavy growth (60-100 %) of microbial on the specimen. The antibacterial activity of these resins at the end of three weeks ispresented in TABLE 6. The obtained data indicate that the modified alkyd resin with2,2\-Di-thiosalicylic acidshowsantibacterial activity if compared with the unmodified resin. Also, this activity increased by increas-

TABLE 6 : Antibacterial activity of the newly synthesized alkyd resins

Resin No.	Excess-OH (%)	Bacillus subtils ATCC 7972	Staphylococcus Aureus NCTC 7447	Ascherichi Coli NCTC 10416	Pseudomona aeruginosa ATCC 10145	Candida Albicans IMRU 3669	Aspergillus Niger ATCC 6275
I_a	0	4	4	4	4	4	4
I_b		3	3	3	3	3	4
I_c		2	2	2	3	3	4
I_d		2	2	2	2	2	3
II_a	10	4	4	4	4	4	4
II_b		3	3	3	3	3	4
II_c		2	2	2	2	2	4
II_d		1	1	1	2	2	3
III_a	20	4	4	4	4	4	4
III_b		2	2	2	3	3	4
III_c		2	2	2	2	2	3
III_d		1	0	1	1	2	2
IV_a	30	4	4	4	4	4	4
IV_b		2	2	2	2	2	4
IV_c		1	1	2	2	2	3
IV_d		0	0	1	0	1	2

ing the modifier percent and the hydroxyl content in the resin.

CONCLUSION

The suitability of 2,2\ -Di-thiosalicylic acid in the modification of alkyd resin was evaluated. The varnishes characteristics (such as viscosity, air drying and stoving), the mechanical properties (gloss, flexibility, hardness, and adhesion) increased as the modifier content and the hydroxyl group contents in the backbone increased. This is attributed to the decrease solubility of the alkyd in the solvent (xylene) as oil content decreases, increasing the amount of solvent embedded in the alkyd resin. It has been reported that higher oil content of long and medium oil alkyds gave slower initial drying due to more thermosetting of long oil alkyd as compared to short oil alkyd[5,12]. Subsequently, gloss and hardness retentions are more pronounced in short alkyd compared to the medium and long oil alkyd. Also, the resistance of the modified alkydsin different service media shows an excellent properties especially at higher 2,2\-Di-thiosalicylic acid and hydroxyl group contents. This may be due to the fact that alkyds are essentially polyesters that are susceptible to hydrolysis, in addition to, increase the aromatic ring added on it sulphur atom.

The promising results obtained from antibacterial activity of the modified alkyds can be attributed to introducing an aromatic rings and active atom such as sulphur added on the aromatic ring to the backbone enhance the biological activity of the resin[13-14]. Also, the presence of an electron–rich sulphur atom is beneficial for this resin which can penetrate the bacterial cells by suitable binding[14-16].

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