



DIMER FATTY ACID-MODIFIED POLYESTERAMIDE RESIN COMPOSITIONS

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Abstract

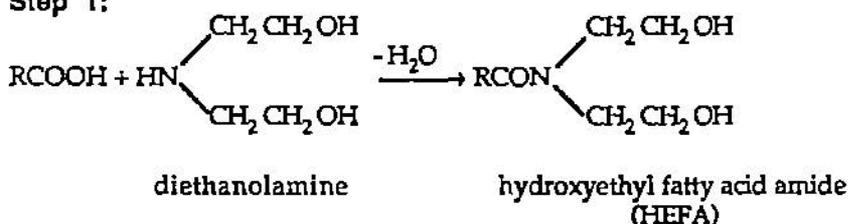
The article deals with the preparation of dimer fatty acid-modified polyesteramide resin. The fatty acids or oils used were: linseed, dehydrated castor oil, soyabean, rice germ and tall oils. Various varnish compositions of the same resin constants were prepared. Evaluation studies indicated that the presence of dimer linseed oil or dehydrated castor oil fatty acids is essential. The presence of rosin in such formulations leads to compositions of excellent performances.

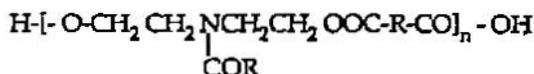
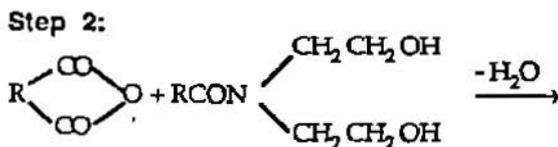
Introduction:

Polyesteramide resins combine the properties of both polyester and polyamide resins. Their preparation and evaluation in the field of surface coatings were reported by Gast *et al.* (1-3) and Naser *et al.* (4-6).

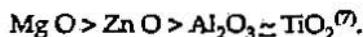
The modified-method of formation involves firstly the formation of hydroxyethyl fatty acidamide, which is considered as the polyhydric source, followed by condensation with polybasic acid or anhydride in a manner similar to alkyd formation. The solvent technique was used to avoid the formation of dark-coloured resins. The sequence of formation is represented by the following series of equations:

Step 1:





Recently, the effect of the presence of catalyst on the reaction of diethanolamine and fatty acid was studied and the catalysts were arranged in the following order of reactivity:



Dimer acids is the general term applied to products obtained by the intermolecular reaction of two or more molecules of unsaturated fatty acid esters. For the most part, the unsaturated fatty acids used commercially in manufacture are those which have 18-carbon atoms and are mixtures of oleic and linoleic acids. Dimerization of unsaturated fatty acids has been claimed to lead to cyclic structures by a Diels-Alder reaction, and to linear dimers and higher oligomers by a free-radical route involving hydrogen transfer, particularly in the presence of oxygen⁽⁸⁾.

Most of the prepared polyesteramides of the conventional types and no published work was traced concerning the preparation of modified polyesteramides.

This article deals with the preparation of various dimer fatty acid-modified polyesteramide resins.

Experimental

Materials used:

All chemicals and solvents used throughout the whole investigation were of the purest grade available.

The soyabean and rice germ oils were commercial oils purchased from the local market. The dehydrated castor, linseed and tall oil fatty acids were kindly provided from the Egyptian Paint Company.

Methods of Preparations:

Preparation of hydroxyethyl fatty acidamide (HEFA)⁽⁷⁾:

1. A mixture of freshly distilled diethanolamine (0.11 mole), fatty acid (0.1 mole), 15-20 ml xylene and MgO catalyst (0.2 mole/100 gm resin) were placed in 250 ml R.B. flask fitted with a Dean and Stark apparatus.

The contents were heated up to reflux until the theoretical amount of water was approximately collected. The reaction mixture was cooled, filtered and kept in well-closed container.

Preparation of polyesteramide resin:

The hydroxyethyl fatty acidamide previously prepared was heated with acid anhydride or dibasic acid according to the calculated weight (Table 1). The esterification was followed by observing the amount of liberated water.

The following abbreviations were used throughout the test:

1. Hydroxyl components:

HELFA: Hydroxy-ethyl linseed oil fatty acidamide.

HEDCFA: Hydroxy-ethyl dehydrated castor oil fatty acidamide.

HERGFA: Hydroxy-ethyl rice germ oil fatty acidamide.

DEA: Diethanolamine.

G: Glycerol.

E.G.: Ethylene glycol.

DEA/rosin: Dihydroxy diethylamine derivative of rosin.

2. Carboxyl component:

PA: Phthalic anhydride.

DLFA: Dimer linseed fatty acid.

DSBFA: Dimer soyabean fatty acid.

DTFA: Dimer tall fatty acid

DDCFA: Dimer dehydrated castor fatty acid.

DCOFA: Dehydrated castor oil fatty acid.

Table 1: Weight charge compositions

No.	Hydroxyl component			Carboxyl component		
	Ingredient	W g.	%*	Ingredient	W g.	%*
I	HELFA	55.4	100	DLFA	76.7	100
II	HEDCFA	14.4	30	PA	12.1	60
	G	5.8	60	DLFA	23.1	30
	PE	1.6	10	DSBFA	7.7	10
III	HELFA	14.4	30	PA	12.1	60
	G	5.8	60	DLFA	23.0	30
	PE	1.6	10	DSBFA	7.7	10
IV	HELFA	14.4	30	PA	12.1	60
	G	5.8	60	DLFA	7.7	10
	PE	1.6	10	DSBFA	23.1	30
V	HELFA	23.1	40	PA	15.2	75
	E.G	5.8	60	DLFA	9.5	12.5
				DSBFA	9.5	12.5
VI	HELFA	23.1	40	PA	15.2	75
	G	5.8	60	DLFA	9.5	12.5
				DSBFA	9.5	12.5
VII	HEDCFA	23.1	40	PA	15.2	75
	G	5.8	60	DLFA	9.5	12.5
				DSBFA	9.5	12.5
VIII	HEDCFA	23.1	40	PA	15.2	75
	G	5.8	60	DLFA	9.5	12.5
				DTFA	9.5	12.5
IX	HERGFA	23.1	40	PA	15.2	75
	G	5.8	60	DLFA	14.25	12.5
				DDCFA	4.75	12.5
X	HERGFA	23.1	40	PA	15.2	75
	G	5.8	60	DLFA	9.5	12.5
				DSBFA	9.5	12.5
XI	HERGFA	23.1	40	PA	15.2	75
	G	5.8	60	DLFA	6.3	8.3
				DTFA	6.3	8.3
				DDCFA	6.3	8.3
XII	HEDCFA	14.4	20	PA	15.2	75
	G	7.3	80	DLFA	9.5	12.5
				DSBFA	9.5	12.5
XIII	HEDCFA	23.1	40	PA	15.2	75
	G	4.8	60	DLFA	9.5	12.5
				DSPFA	9.5	12.5
XIV	HEDCFA	25.9	45	PA	15.2	75
	DEA/Rosin	3.4	5	DLFA	9.5	12.5
	G	4.8	50	DSBFA	9.5	12.5
XV	HEDCFA	23.1	40	PA	15.2	75
	DEA/Rosin	6.6	10	DLFA	9.5	12.5
	G	4.8	50	DSBFA	9.5	12.5
XVI	DEA	8.4	60	PA	15.2	58
	G	4.8	40	DCFA	20	20
				ROSIN	2.7	2
				DLFA	9.5	10
				DSBFA	9.5	10
XVII	DEA	8.4	60	PA	15.2	56
	G	4.8	40	DCOFA	18	20
				ROSIN	5.4	4
				DLFA	9.5	10
				DSBFA	9.5	10

* Based on total acid equivalent

2. Liberation of fatty acids:

Soyabean or rice germ oils (0.1 mole; 90 g) were refluxed in Erlenmeyer flask with alcoholic potassium hydroxide (0.3 mole; 16.8 g). The contents were gently boiled under reflux until complete saponification. The contents were transferred to a separating funnel and the unsaponifiable matter was extracted with diethyl ether. The aqueous layer contained the saponifiable matter was acidified using hydrochloric acid and the free fatty acids was extracted with ether and dried over anhydrous sodium sulfate, filtered, and evaporated under vacuum.

3. Preparation of methyl esters:

The oils or fatty acids were refluxed in dry absolute methanol in the presence of NaOH or conc. H_2SO_4 for the oils or fatty acids respectively. The refluxing was continued till complete esterification. Excess methanol was removed by distillation, and the methyl esters was dried over P_2O_5 .

The methyl esters were identified on thin-layer chromatographic plates coated with silica gel G using petroleum ether-diethyl ether 80:20 as developing solvent. The esters gave a well defined single spot (R_f 0.72).

4. Preparation of dimer-fatty acids (DFA)⁽⁹⁾:

The methyl esters (400 g) were charged with (0.12 g) anthraquinone in a one litre three-necked round bottom flask fitted with thermometer, air condenser and an inlet for nitrogen. The reaction mixture was heated at (300°C) for (16 hours). A stream of oxygen-free dry nitrogen was maintained throughout the heat treatment to prevent oxidation.

The polymerized esters were distilled from standard claisen flask fitted with a short fractionating column. Distillation was carried out at (4 mm/Hg) while bubbling in a stream of oxygen-free dry nitrogen to prevent bumping, and to avoid oxidation. The fraction boiling at (220°C) was collected.

5. Methods of Evaluation:

Acid value, iodine value, drying time, resistance against water, acid, alkali were conducted according to the standard method.

6. Instrumental analysis:

Gas-liquid chromatographic analysis for the identification of fatty acids of rice germ oil and tall oils was carried out at the central laboratory, Faculty of Science, Cairo University on a Pye-Unicam apparatus using DEGA column with the following conditions:

Column temperature 180°C.

Detector temperature 240°C.

Injection temperature 230°C.

Attenuation 8×10^{-3} .

It should be noted that the fatty acid determination of rice germ oil was carried out before and after cooling at 5°C for 24 hrs, in order to separate the saturated acids.

Results and Discussion:

Literature survey concerning the modification of the recently introduced polyesteramide resins for surface coating is scanty. This aspect together with the availability of some semi-drying oils are the main target of the investigation.

The rice germ and tall oils were subjected to fatty acid identification using GLC technique. The data obtained are tabulated in table 2 together with those of D.C.O., linseed⁽¹⁰⁾ and soyabean oil⁽¹¹⁾. Also the acid and iodine values of rosin were determined and was found to be equal to 162 mg KOH and 22 cc. I₂ respectively.

Medium oil-length soyabean modified alkyds is amongst the conclusions drawn from recently published work⁽¹¹⁾. The resin characteristics were also adapted in this investigation. After many unsuccessful trials, the following resin constants were achieved: [acid equivalent: 0.273, base equivalent 0.312] and were used all over the whole investigation.

Table 2: Fatty acid % compositions of the used oils

Fatty acids	Tall oil	Rice germ		D.C.O.	Linseed	Soyabean
		Uncooled	Cooled at 5°C			
Palmitic	1.38	18.01	16.63	} 6%	} 6-11	} 17.84-23.6
Stearic						
Oleic	40.93	44.58	38.29	6%	13-29	28.22-30.2
Linoleic	50.20	37.41	42.89	2%	17-30	42.52-50.6
Linolenic	7.49	—	2.19	—	47-55	3.16-3.25
Ricinoleic	—	—	—	86%	—	—

The prepared resins were thinned with mineral terepentin to 40% solids, filtered and the drier combination were added (Mn and Co

naphthenate; 0.03 per cent based metal/resin)⁽¹¹⁾. Preliminary evaluation of the film performance were conducted and the data are given in table 3.

Table 3: Resin Characteristics Preliminary Evaluation.

Resin No.	Drying time		Remarks
	Air drying in hours	Stoving at 105°C for 15 minutes	
I	Non-drying	Non-drying	Unsuccessful film performances.
II	Non-drying	Non-drying	Separation of two layers.
III	Non-drying	Non-drying	Separation of two layers.
IV	Non-drying	Non-drying	Separation of two layers.
V	4	O.K.	Excellent film appearance
VI	4	O.K.	Excellent film appearance
VII	3	O.K.	Excellent film appearance
VIII	3	O.K.	Excellent film appearance
IX	Non-drying	Non-drying	Residual film tackness
X	Non-drying	Non-drying	Residual film tackness
XI	3	O.K.	Excellent film performance
XII	3	O.K.	Excellent film performance
XIII	3	O.K.	Excellent film performance
XIV	3	O.K.	Excellent film performance
XV	3	O.K.	Excellent film performance
XVI	Non-drying	Non-drying	Separation of two layers
XVII	Non-drying	Non-drying	Separation of two layers

The main conclusion drawn from the above record of data clearly indicates the modifying power of the presence of dimer fatty acids of linseed and dehydrated castor oils, in polyesteramide resins.

From table 2 and 3, it can be concluded that

- a) Blank experiments (I) composing of hydroxyethyl linseed fatty acidamide and dimer linseed fatty acids produced resins of unsatisfactory resin characteristics.
- b) The incorporation of PE in resin compositions (II-IV) leads to the separation of two heterogenous phases compositions. Therefore (I-IV) are rejected from further investigation.
- c) Replacement of PE by E.G. or G. leads to compositions of better resin characteristics, if it used in HEFA: G or EG ratio as 40:60 based on total acid equivalent and contains linseed oil fatty acids.
- d) Compositions containing rice germ oil fatty acids showed unsatisfactory results (No IX and X), except composition No. XI where L.O., T.O. and D.C.O. dimer fatty acids are incorporated.
- e) The presence of the fatty acids of L.O., S.B.O., D.C.O. or T.O. or their compositions leads to formulations of satisfactory results XI, XII and XIII.
- f) Employing the hydroxyethyl dehydrated castor oil fatty amid in resin formulations with DFA of L.O., S.B. oil fatty acids showed satisfactory properties (No. XII, XIII; HEDCFA% 20 and 40% respectively).
- g) Partial replacement of HEDCFA by hydroxyethyl amide of rosin (5-10% of the total hydroxyl equivalent) greatly improves the resin characteristics (No. XIV, XV), especially the gloss of the films.

Trials to indicate the effect of order of addition in the previous formulations (No. XIV, XV), showed no significant improvements. As a matter of fact, unsatisfactory resin performance are obtained (No XVI, XVII).

Further evaluation of satisfactory compositions of (VI, VII, VIII, XI, XII, XIII, XIV and XV) was conducted. The data obtained are given in table 4.

Table 4: Film Performance Data, the Effect of Water, Acid and Alkali

Resin No.	Cold water		Boiled water		Acid		Alkali	
	Air drying	Stoving	Air drying	Stoving	Air drying	Stoving	Air drying	Stoving
VI	Ex	Ex	G	Ex	P	G	G	G
VII	Ex	Ex	G	Ex	Ex	Ex	G	G
VIII	G	Ex	G	Ex	Ex	Ex	G	G
XI	G	Ex	Ex	Ex	G	G	G	G
XII	Ex	Ex	Ex	Ex	G	G	G	G
XIII	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
XIV	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
XV	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex

Ex; mean excellent; unaffected

G; mean good; slightly affected.

P; mean poor; affected

The data given in table 4 clearly indicate the following generalizations:

1. The presence of dimer linseed oil fatty acids is essential.
2. The presence of hydroxyethyl dehydrated castor fatty amide/glycerol greatly improves the film performances of the produced resins.
3. The incorporation of dihydroxy diethylamide derivatives of rosin and dehydrated castor oil fatty acids with the dimer fatty acids of linseed and soyabean oils leads to resins of outstanding film performances.

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**راتنجات البولى استرايميد المطوره
بدايمر الأحماض الدهنية**

عفاف أحمد برعى

قسم الكيمياء - كلية العلوم - جامعة الأزهر فرع البنات

مدينة نصر - القاهرة - مصر

استهدف البحث دراسة عدد من تركيبات ورنيشية للبولى استر أميد لدائمرات الأحماض الدهنية الغير مشبعة التى تحتوى على ١٨ ذرة كربون وذلك عن طريق تحضير هيدروكس إيثل أميدات هذه الأحماض تم تكثيفها مع أحماض أو أنهيدريدات عديدة القاعدية ، وظهرت نتائج التقييم ان الراتنجات المحتوية على دايمر أحماض زيت بذر الكتان وكذلك دايمر أحماض زيت الخروع المنزوع الماء اساسى للتحضيرات التى اعطت نتائج مشجعة . كما تم التوصل لنتائج ممتازة عند استعمال مشتقات الداى هيدروكسى إيثل أميد راتنج التلقونية فى وجود أحماض زيت الخروع المذكور وزيت بذر الكتان .