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# DIMER FATTY ACID-MODIFIED POLYESTERAMIDE RESIN COMPOSITIONS

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## Abstract

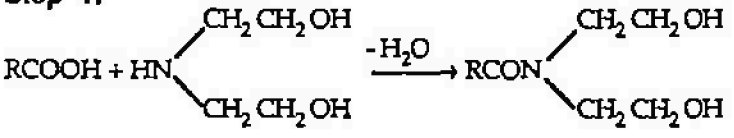
The article deals with the preparation of dimer fatty acid-modified polyesteramide resin. The fatty acids or oils used were: linseed, dehydrated castor oil, soyabean, rice germ and tall oils. Various varnish compositions of the same resin constants were prepared. Evaluation studies indicated that the 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].

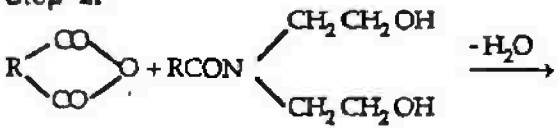
The modified-method of formation involves firstly the formation of hydroxyethyl fatty acidamide, which is considered as the polyhydric source, followed by condensation with polybasic acid or anhydride in a manner similar to alkyd formation. The solvent technique was used to avoid the formation of dark-coloured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

**Step 1:**



diethanolamine — hydroxyethyl fatty acid amide (HEFA)

Step 2:



$$H\text{-}[\text{-}O\text{-}CH_2CH_2N(COR)CH_2CH_2OOC\text{-}R\text{-}CO]_n\text{-}OH$$

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:

$$MgO > ZnO > Al_2O_3 \simeq TiO_2$$ [7].

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 structurs 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 purcashed from the local market. The dehydrated castor, linseed and tall oil fatty acids were kindely 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.

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## 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 |
| | | 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 tansfered 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 vaccum.

## 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 qvoid 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:

Colum temperature 180°C.

Detector temperature 240°C.

Injection temperature 230°C.

Attenuation $8 \times 10^{-3}$.

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 eq. $I_2$ 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<br>Stearic | 1.38 | 18.01 | 16.63 | } 6% | } 6-11 | } 17.84-23.66 |
| Oleic | 40.93 | 44.58 | 38.29 | 6% | 13-29 | 28.22-30.27 |
| Linoleic | 50.20 | 37.41 | 42.89 | 2% | 17-30 | 42.52-50.69 |
| 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 |

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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 incoporation 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 استرأميد المطوره
## بدايمر الأحماض الدهنية

عفاف أحمد برعى
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استهدف البحث دراسة عدد من تركيبات ورنيشية للبولى استر أميد لدايمرات الأحماض الدهنية الغير مشبعة التى تحتوى على ١٨ ذرة كربون وذلك عن طريق تحضير هيدروكس ايثيل أميدات هذه الأحماض تم تكثيفها مع أحماض أو انهيدريدات عديدة القاعدية . واظهرت 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 إيثيل أميد راتنج القلفونية فى وجود أحماض زيت الخروع المذكور وزيت بذر الكتان .