
**VARIOUS MODIFIED POLYESTERAMIDE VARNISHES AS
ANTIMICROBIAL SURFACE COATING VEHICLES.**

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Abstract

New modified polyesteramide compositions were prepared and evaluated as vehicles for surface coating Resin was prepared by partial replacement of hydroxyl ethyl fatty acid amide (HEFAA) using 6,8-Dibromocumarin-3-N-bis(2-hydroxyethyl) carboxamide which carried out by solvent technique, This modification, as expected, improved the film performance and durability and lead to substantial antimicrobial growth control.

Key word: Polyester amide, Surface coating , Biological activity, Antimicrobial varnishes, Protective coating, Biocide activity of organic coating.

Introduction

Polymeric systems based on polyesteramides (PEA) are high performance material, which combine the useful properties of polyester and polyamide resins, and finds many applications most importantly as protective surface coatings [1,2]. Diethanolamine derivatives of fatty acids were used in the preparation of polyesteramide and alkyd/ polyesteramide resins [3]. Most alkylolamides are derived from ethanolamine and fatty acids [4, 5]. The above-mentioned derivatives are used as the ingredient source of dihydric alcohol followed by poly condensation.

Polyesteramide resins containing pentachlorophenol residue in their structure were prepared and evaluated as antimicrobial growth control [6]. Another polyesteramide resins were prepared containing a stoichiometric amount of 8-hydroxquinoline as preservative against micobiological attack [7]. The other modified polyesteramide resins were prepared in which stoichiometric amount of hydroxyethyl fatty acid amides are replaced by nicotinic and isonicotinic acids derivatives of diethanolamine and triethanolamine. Such resin compositions exhibited antimicrobial growth control [8]. A new modified polyesteramide resins were screened for their anti-bacterial activity against E coli, Pseudomonas sp, and staphylococcus sp, and their antibacterial activity was evaluated in the nutrient agar media [9].

In this investigation the chemical incorporation of the biocide in the resins molecules is the main idea which can be achieved by partial replacement of polyols

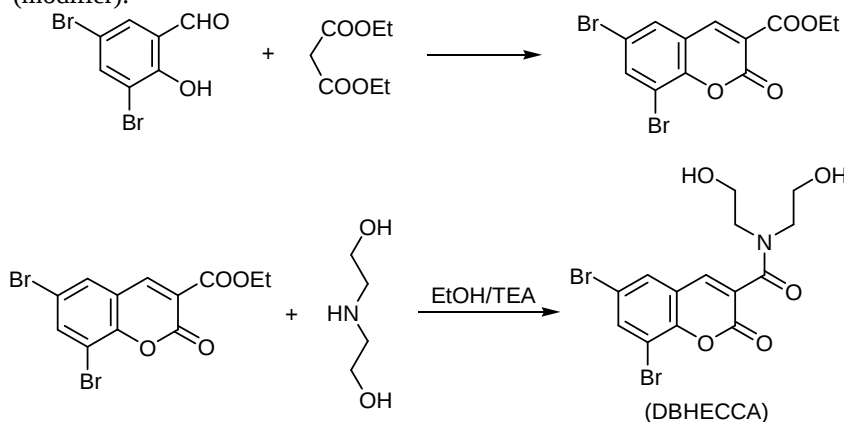
used in the manufacture of polyesteramide resins by 6,8-Dibromo coumarin-3-*N*-bis-(2-hydroxyethyl) carboxamide (modifier). Such modification introduce the biologically active nuclei in the structure of the resin and consequently would expect to affect their biological activity.

Experimental

All solvents and chemical used through the whole investigation were at least of chemically pure grade, except where mentioned.

Methods of Preparations

I. Preparation of 6,8-Dibromo coumarin-3-*N*-bis-(2-hydroxyethyl) carboxamide (modifier).



A mixture of 6,8-Dibromocoumarin-3-ethyl carboxylate (0.1 mole) and (0.1 mole) of freshly distilled diethanol-amine was refluxed for 5 hrs. in presence of absolute ethanol as a solvent and triethylamine as base , The product obtained was identified as 6,8-Dibromocoumarin-3-*N*-bis-(2-hydroxyethyl) carboxamide (modifier).

II. Preparation of various modified Polyesteramide Resins;

The preparation of various modified polyesteramide resins were carried out in two general steps:

A. Preparation of *N,N*-bis(2-hydroxyethyl)linseed oil fatty acids amide (HELA):

A mixture of freshly distilled diethanolamine, DEA (10.5gm, 0.1 mole) and linseed oil fatty acid (0.28 gm, 0.1 mole) was placed in 250 ml round-bottomed flask fitted with Dean and Stark apparatus. The mixture was allowed to reflux until approximately the theoretical amount of water (1.8ml, 0.1 mole) was collected,

indicating the complete formation of *N,N*-bis(2-hydroxyethyl) linseed oil fatty acids amide (HELA).

B. Preparation of Modified Polyesteramide Resins:

Formulations containing *N,N*-bis(2-hydroxyethyl)linseed oil fatty acids amide (HELA) and or 6,8-Dibromocumarin-3-*N*-bis(2-hydroxyethyl) carboxamide (modifier)" as the ingredient source of the polyol used, and phthalic anhydride (PA) as the polybasic ingredient were prepared by solvent technique. The reaction was followed by observing the amount of water liberated versus time.

Table (1) : Resin characteristic constant of variouse modified polyesteramide resins.

Ex-OH	e _o	e _A	e _B	R	H ₂ O ml off
0%	0.519	0.259	0.260	1.00	2.3
10%	0.573	0.273	0.300	1.10	2.3
20%	0.650	0,298	0.352	1.20	2.3
30%	0.779	0.339	0.440	1.30	2.3

e_o :Total Equivalentents Present at the start of reaction, e_A: Number of acid equivalentents,
 e_B : Number of Hydroxyl Equivalent, R : Ratio of total-OH groups to total-COOH groups(e_B/ e_A),

Resin Preparations:

The resins were prepared by using linseed oil fatty acids via solvent process, using Dean and stark apparatus, covering a wide range of oil lengths and hydroxyl content (0, 10, 20, and 30%Excess-OH).within each formulation, the total number of acid and hydroxyl equivelant were kept constant, and the various hydroxyl equivelant (e_B) of each type of Excess-OH resinare listed in table (2).

Table (2): List of hydroxyl equivelant of various modifications.

Number	HELA	Modifier
*A	1.00	00.0
B	0.90	0.10
C	0.80	0.20
D	0.70	0,30

*Unmodified formulations (A) was included comparison

Methods of evaluation:

Methods of testing and evaluation were performed according to the American standard test methods and including, acid value [10], hydroxy value [11], solid content [12], preparation of test panels [13], drying time [14], viscosity [15], color [16], The pencil hardness [17], film thickness [18], adhesion [19], Gloss [20], flexibility [21], chemical resistance [22-25].

Microbiology Assay

The preparation of test specimens; procedure and evaluation of the results were conducted according to standard methods [26,27].

Results and Discussion

Recently new modified polyesteramide resins were described through the partial replacement of *N,N*-bis(2-hydroxyethyl)linseed oil fatty acids amide (HELA) by 6,8-Dibromocoumarin-3-*N*-bis(2-hydroxyethyl) carboxamide (modifier), such modification showed better film performances and leads to the formation of biological active polyester-amide resins.

The modifier 6,8-Dibromo-*N,N*-hydroxyethylcoumarin carboxamide, was prepared through the reaction of 6,8-Dibromocoumarin-3-ethyl carboxylate with diethanolamine in presence of triethylamine as base. The structure of the modifier was elucidated on the basis of the following.

1- Hydroxyl value 2- IR spectrum 3- ¹HNMR spectrum .

- (1) Hydroxyl Value 253 mg. KOH/gm. (Theo. 257.9 mg. KOH/g,
- (2) The IR spectrum (Fig. 1), showed the following absorption bands: 3402 cm⁻¹ (OH), 3064 cm⁻¹ (C-H-arom.) 2806-2980 cm⁻¹ (CH-aliph.), 1208,11 cm⁻¹ 64 (COO) in six member ring, and 1764, 1778 cm⁻¹ (C=O) and 1608 cm⁻¹ (C=N).

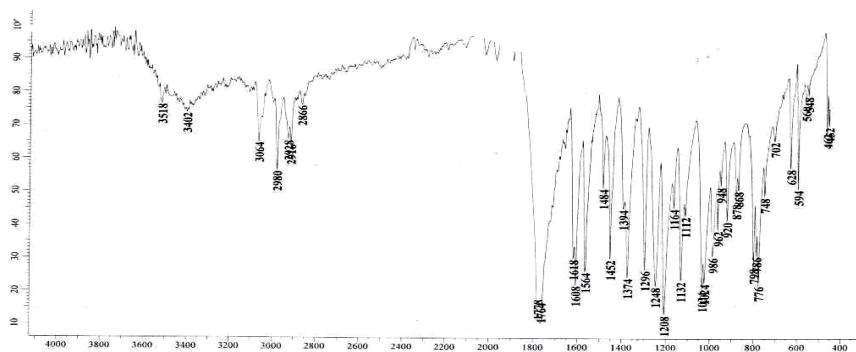


Fig (1): IR Spectra of 6,8-Dibromocoumarin-3-*N*-bis-(2-hydroxyethyl) carbox amide [DBHECCA]

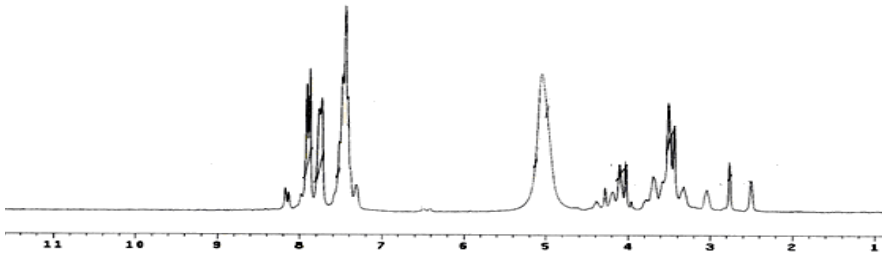


Fig.(2): ¹H NMR Spectra of 6,8-Dibromocoumarin-3-N-bis-(2-hydroxyethyl)carboxamide.

3) ¹H NMR spectrum (Fig. 2) was measured in DMSO-d₆ and showed signals at δ = 2.7 ppm (t, 4H, 2CH₂-N), 4.2 (t, 4H, 2CH₂-OH), 5.0 (hump, 2H, 2OH), and 7.4-8.2 ppm (m, 3H, Ar-H).

During the course of the preparation, the amount of water collected in the trap was observed against time of the reaction and the data obtained are graphically represented in fig (3)

Reaction
time
min

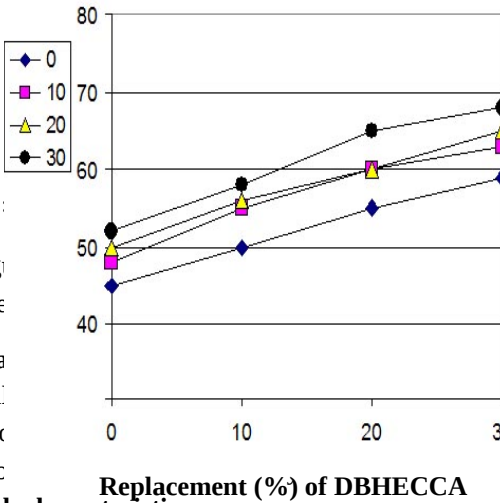


Fig (3) :

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Varnish characteristics:

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The characteristics of various varnishes were determined and the data are shown in Table (3)

Table(3): Effect of Dibromocoumarin carboxamide upon varnish characteristics.

Resin No.	Excess-OH (%)	Replacement (%) Of DBHECCA	Viscosity (Gardnar)	Color (Gardnar)	Air drying time(h)	Stoving at 110C(60-90min)	Stoving at 120C(1hr)
IA	0	0	D	>18	5	T	VST
B		10	F	>18	3.30	ST	60
C		20	H	>18	2.50	VST	60
D		30	J	>18	2.0	HD	30
II A	10	0	E	>18	5.0	ST	VST
B		10	G	>18	3.50	VST	HD
C		20	I	>18	2.0	HD	HD
D		30	L	>18	2.0	HD	HD
IIIA	20	0	H	>18	4.0	ST	VST
B		10	I	>18	2.50	HD	HD
C		20	L	>18	2.0	HD	HD
D		30	N	>18	1.50	HD	HD
IvA	30	0	P	>18	4.0	VST	HD
B		10	L	>18	2.50	HD	HD
C		20	P	>18	2.0	HD	HD
D		30	T	>18	1.50	HD	HD

T : Tackiness, ST:Slightly tackiness, VST:very slightly tackiness, HD: hard dry

Film performance . A-

From the data recorded in table (3), the following conclusions were drawn

1. The color of the prepared modified resins was dark brown (>18in Gardner scale) due to the presence of nitrogenous base.
2. Viscosity of varnishes increases through the addition of the modifier.
3. Air drying and stoving time are decreased by increasing the amount of the modifier.

Mechanical properties and extensive chemical resistance of dried films:

The dry film characteristics of the various modified resin films were carried out according to standard methods and well- known techniques and the results are tabulated in Tables (4).

Table (4) Varnish and Film Characteristic of Various Modified Polyesteramide Resins

Resin No.	Film Thickness μ		Gloss at 20°C		Scratch Hardness Per (Kg)		Flexibility	Adhesion	Water Resistance Per(day)	Acid * Resistance Per(day)	Alkali ** Resistance Per(day)	Solvent Resistance Per(day)
	a	s	a	S	a	S						
1a	31	30	90	85	>1kg	>1.5kg	Pass	5B	20	18	1	>30
b	33	30	93	90	>1kg	>1kg	pass	5B	24	24	3	>30
c	34	30	93	93	>1.2kg	>1.5kg	Pass	5B	>30	30	5	>30
d	34	32	94	94	>1.3kg	>1.5kg	Pass	5B	>30	30	7	>30
1la	32	30	90	90	>1.2kg	>1.5kg	Pass	5B	21	24	5	>30
b	33	31	93	92	>1.4kg	>1.5kg	Pass	5B	30	24	7	>30
c	36	32	94	95	<2.00kg	<2.00kg	Pass	5B	>30	30	7	>30
d	36	31	95	96	<2.00kg	<2.00kg	Pass	5B	>30	>30	9	>30
1lla	32	31	92	90	>1.5kg	>1.5kg	Pass	5B	>30	26	5	>30
b	32	31	94	94	>1.5kg	<2.00kg	Pass	5B	24	30	7	>30
c	35	32	95	95	<2.00kg	<2.00kg	Pass	5B	30	>30	7	>30
d	35	33	95	97	<2.00 kg	<2.00kg	Pass	5B	>30	>30	9	>30
1va	33	32	93	92	>1.41kg	>1.5kg	Pass	5B	26	30	7	>30
b	35	33	94	94	>11.5kg	<2.00kg	Pass	5B	>30	>30	9	>30
c	36	34	96	94	>2.00kg	<2.00kg	Pass	5B	>30	>30	9	>30
d	37	34	96	96	>2.00kg	<2.00kg	Pass	5B	>30	>30	11	>30

Acid concentration (H₂SO₄) 10% by weight
 Alkali concentration (Na₂CO₃) 5% by weight

The main conclusion drawn from the water, acid, alkali and solvent resistances data for the various, modified polyesteramide resins tabulated in Table (4) indicate the following generalizations:

1. The modified films show outstanding performance compared with unmodified films.
2. Stoved films exhibit better water, acid and solvent resistances compared with air-dried films.
3. Increasing the percentage of modifier leads to a substantial improvement in the film resistances towards water and acid.
4. The solvent resistance of all examined films are excellent and it is not able to show the effect of the modifier
5. The effect of the various modifications on the alkali resistance is clearly shown. Increasing the percentage of modification leads to better improvement in the alkali resistances of the air-dried and stoved films. Also, increasing the excess hydroxyl content of the resin greatly improves the alkali resistances of the film.
6. All films passed successfully the flexibility and adhesion tests.
7. The scratch hardness and the gloss of dried films are improved by increasing the amount of modifier.

Antimicrobial Activity of Various Modified Polyesteramid Resins:

Microbiological activity of the modified resins was carried out on liquid varnish and dried films, the data are recorded in Tables (5).

Evaluation of results:

The results in Tables (5) are identical similar, the various modified polyesteramide resins in different substitutions showed the same effect in liquid solution as in solid film .The modification of present formulations of polyesteramide resins by the modifier increase the antimicrobial activity against the target microorganisms. on the other hand, the increasing the Excess -OH %, leads to increasing of the antimicrobial activity, i.e, 30% Excess-OH > 20% Excess-OH \geq 10% Excess -OH > 0% excess-OH.

It is noteworthy to mention that, the unmodified polyesteramide resins (formulations "a"), are completely inactive against the microorganisms under investigation.

Table (5) : Antimicrobial Activity of Various modified Polyesteramide Resins

Resin No.	Bacillus Subtilis ATCC 7972		Staphylococcus Aureus NCTC 7447		Ascherichi Coli NCTC 10416		Pseudomonas Aeruginosa ATCC 10145		Candida Albicans IMRU3669		Aspergillus Niger ATCC 6275	
	V	DF	V	DF	V	DF	V	DF	V	DF	V	DF
Ia	4	4	4	4	4	4	4	4	4	4	4	4
b	3	3	3	3	3	3	3	3	3	3	3	3
c	2	3	2	2	2	2	2	2	2	2	2	3
d	1	2	1	1	1	1	1	1	1	1	2	2
Ia	4	4	4	4	4	4	4	4	4	4	4	4
b	3	3	2	3	3	3	2	3	3	3	3	3
c	1	2	1	2	1	1	1	2	2	2	2	2
d	0	1	0	0	0	0	0	1	1	1	1	2
IIIa	4	4	4	4	4	4	4	4	4	4	4	4
b	2	3	2	3	2	3	2	3	2	3	3	3
c	1	1	0	1	1	2	1	1	1	2	2	2
d	0	0	0	1	0	0	0	0	0	1	1	1
IVa	4	4	4	4	4	4	4	4	4	4	4	4
b	2	2	2	2	2	2	1	2	2	2	3	3
c	0	0	0	0	0	1	0	1	1	1	2	2
d	0	0	0	0	0	0	0	0	0	0	1	1

Ia, IIa, IIIa and IVa mens unmodified samples .

V means Varnish in Wet State, and DF means dry film.

0 mens high performance antimicrobial activity

4 means inactive sample against the microorganism.

Reference

1. L.E,Gast, W.J. Schneider, G.E. Mc-Mains, J.C. Cowan, J.Am. Oil. Chem.Soc, 46 (1969) 360.
2. R.N. Mukherjea, K. Pals, S.K.Sinyal, J. Appl. Polym. Sci, 28 (1983).
3. M. Moustafa, Pigment Resin Tech, 21 (12) (1992) 4.
4. A.M.Ramadan, A.Z.Gomma, Euro. Coat, J. 6 (1992) 349.
5. M.Moustafa, I.A. Sabbah, A.M.Naser, F. Abddel-Hai, Pigment&Resin Tech, 16 (12) (1989).4
6. N.M.Taha, M. Moustafa, N.Abdel-Khalik, A.M.Naser, Pigment&Resin Tech, 18 (10) (1989) 4

7. F, Abd El-Hai, and H. M. Mahdy.H.M, *Acta Microbiologica. Et, Immunologica*, 44, (2), 119-131 (1997).
8. Moustafa,M., Abd El-Hai, F., Sabbah, I.A. and Ezz El- Din Mohamed,M, *Al-Azhar Journal of Pharmaceutical Science*, 15, June, ,35-51 (1995).
9. Shahzada Ahmed, Md.Mahfuzul Haque, S.M.Ashraf, Sharif Ahmed, *European polymer Journal*, 40 (2004) 2097-2104
10. ASTM Method: D1639-90 (Reapproved 1996).
11. ASTM Method :D 1957-86 (Reapproved 1995)
12. ASTM Method: D1644-88 (Reapproved 1993).
13. ASTM Method: D3891-96
14. T.K. Rao, V.M. Mannari and D.A. Raval, *J. Sci. Ind. Res.* 55 (1996), pp. 971–980.
15. ASTM Method: D 1545-89 (Reapproved 1993).
16. ASTM Method: D 1544-80 (Reapproved 1989).
17. ASTM Method, D 3363-92a
18. ASTM Method, D 1005-95
19. ASTM Method: D 3359-95a
20. ASTM Method: D 523-89.(Reapproved 1994).
21. ASTM Method, D 522-93a
22. ASTM Method, D 870-92
23. Indian Standard Specification, I.S.158 (1950).
24. Indian Standard Specification, I.S.159 (1950).
25. ASTM Method: D 2792-69 (Reapproved 1993).
26. ASTM method, D 5589-97,(Reapproved 2002), (2004). Vol. 06. 01 (2004).
27. ASTM method, D 5590-94, (Reapproved 2000) Vol. 06.01(2004).