Polyesteramides From Linseed and Soybean Oils for Protective Coatings: Diisocyanate-Modified Polymers[1]

L. E. GAST, WILMA J. SCHNEIDER, G. E. McMANIS and J. C. COWAN,
Northern Regional Research Laboratory,[2] Peoria, Illinois 61604

Abstract

New polymeric coating materials have been prepared by a triethylenediamine-catalyzed reaction of hydroxyl-terminated polyesteramides (HTPA) from soybean or linseed oils with diisocyanates. Eight dibasic acids or anhydrides were reacted with excess N,N-bis(2-hydroxyethyl) fatty amide to yield HTPA; those containing 10 mole per cent excess gave isocyanate-modified polymers with best overall film properties. Reactivity of four diisocyanates with a linseed-HTPA was measured by disappearance of the isocyanate band in the infrared. Depending on chemical composition, structure and curing conditions, films prepared from these polymers have a wide range of drying characteristics, hardness and chemical resistance. Drying times of linseed HTPA-urethane polymer films varied from 0.3 to 48 hr, hardness values (Sward) were from 4 to 70, alkali resistance ranged from 2 to 126 min and the hydrochloric acid and xylene resistances were good to excellent. Impact resistance exceeded 160 in.-lb for all films except two. The soybean-derived polymer films likewise exhibited a wide range of properties; they chiefly differed from linseed-derived films in having greater flexibility and improved alkali resistance.

Introduction

Previously, we described the preparation of polyesteramides from linseed and soybean oils (3,4). The base-catalyzed aminolysis of these oils with excess diethanolamine produced the corresponding N,N-bis (2-hydroxyethyl) fatty amides (HEFA) that were separated from the liberated glycerol and were subsequently reacted with a variety of dibasic acids or anhydrides to give polyesteramides. Films from these polymers have a wide range of properties related to composition. The better polymers dry rapidly to hard chemical-resistant films. Polyesteramides prepared with an excess of HEFA over the dibasic acid contain molecules that terminate primarily in hydroxyl groups (4). This paper describes the preparation and film properties of urethane-polyesteramides from hydroxyl-terminated polyesteramides (HTPA) and diisocyanates.

Experimental Procedures

Urethane-Polyesteramides

Diisocyanate-modified polyesteramides were prepared according to the following general procedure: 5 g of HTPA, 15 g of dry toluene, 17 mg of 8.65% solution of 1,4-diaza-(2,2,2)-bicyclooctane (triethylene diamine) in toluene and an alkyl or aryl diisocyanate (mole ratio of NCO/OH of HTPA = 1) were heated with stirring at 105 C. Attempts to isolate these polymers from solution showed that the last traces of solvent could not be removed from these viscous materials without partial gelation. Therefore, films were prepared directly from the reaction solutions.

Reactivity studies were made with four diisocyanates and linseed-isophthalic HTPA containing 10% excess HEFA. Reactions were carried out as described above. Samples were withdrawn periodically and examined in the infrared to observe disappearance of the NCO band at 2270 cm^{-1}. The results are summarized in Figure 2.

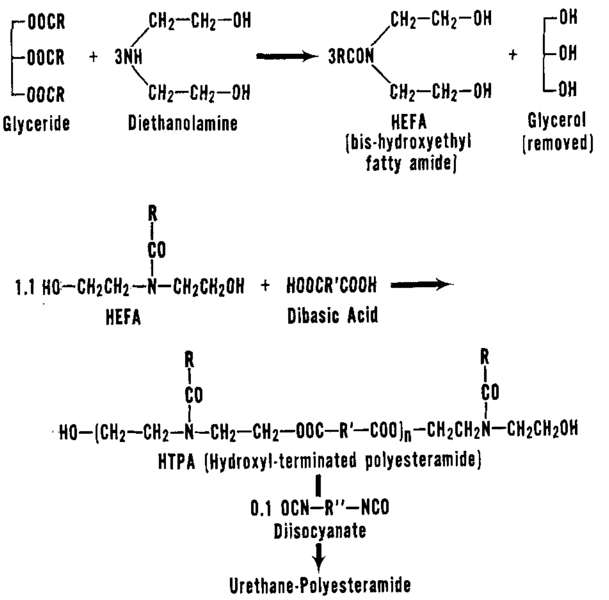


FIG. 1. Synthesis of urethane-polyesteramides from soybean and linseed oils.

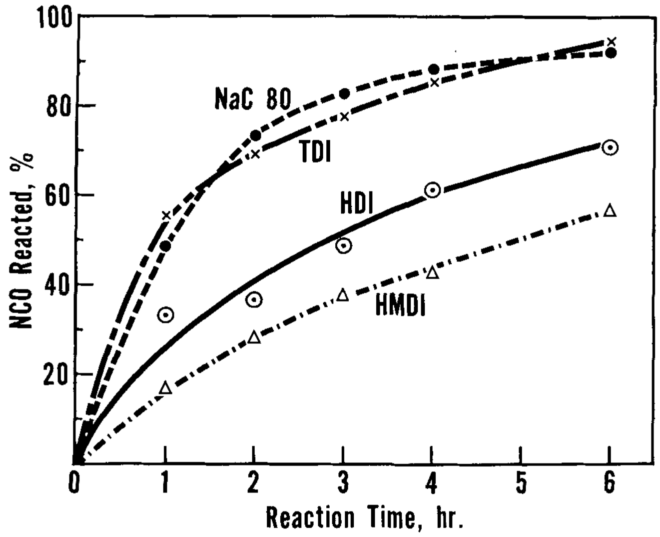


FIG. 2. Reactivity in toluene of diisocyanates with linseed-isophthalic polyesteramide containing 10% excess diol at 105 C. TDI, tolylene-2,4 diisocyanate; HDI, hexamethylene 1,6-diisocyanate; HMDI, 4,4'-methylene bis(cyclohexyl isocyanate); Nacconate 80, mixture of tolylene-2,4- and -2,6-diisocyanate.

---

[1] Presented at American Chemical Society meeting, Chicago, September, 1967.

[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE I
Air-Dried Film Properties of Tolylene Diisocyanate (TDI)-Modified Linseed-Isophthalic Polyesteramides

Urethane-modified HTPA,[a] %	Mol. wt	Drier[b]	Dry-to-touch, min	Tack-free, min	Rocker hardness, days aging			Chemical resistance	
					3	10	24	5% NaOH, min	Xylene, hr
10	5200	+	43	50	56	64	62	16	>192
		—	310	350	36	56	59	18	>192
20	3200	+	13	19	60	71	62	14	>264
		—	73	101	54	74	66	14	>264
30	3500	+	13	15	50	53	60	30	>264
		—	240	280	32	56	60	30	>264

[a] Contains the indicated mole per cent excess of N,N-bis(2-hydroxyethyl) fatty amide (HEFA); HTPA = hydroxy-terminated polyesteramides.
[b] + = Drier (0.5% Pb + 0.01% Co), — = no drier.

Number-average molecular weights in benzene solution were determined with a Mechrolab vapor-pressure osmometer, Model 301. Before molecular weight determinations, all polymers were diluted with benzene and almost all the solvent was removed under vacuum in a rotary film evaporator. This treatment was repeated several times to ensure removal of solvents other than benzene.

Polyurethane-Amides

Polyurethane-amides were prepared from HEFA and an alkyl or aryl diisocyanate as described above. Films were also cast directly from these reaction solutions.

Film Casting and Testing

Chemical resistance, hardness, impact and drying tests were run on films cast on steel Q panels (4 × 8 × 0.032 in.) from a toluene solution containing 25% solids. Drawdowns were made with a drawdown bar machined to give a 4 mil wet film that dried to a thickness of approximately 1 mil. Dried film thickness was measured with a Permascope coating thickness gauge. Films were air dried or baked at 200 C for 10 min with or without a drier (0.5% lead and 0.01% cobalt as naphthenates). Hardness tests were made by the Sward Rocker technique. Chemical and solvent resistance was measured by placing a 1.5 in. diameter watch glass, convex side down, on the surface of the film and introducing the reagent or solvent between the watch glass and film surface. Periodic examination was conducted until the film showed evidence of softening or other deterioration. Dry-to-touch and tack-free times as defined by Gardner (2) were determined on air-dried films by manually placing a small amount of sand on the film periodically.

Impact tests were run with the Gardner impact tester (Cat. No. IG-1120). Films were subjected to direct impact and reverse impact. Films that showed evidence of cracking or loss of adhesion were considered to have failed. The value shown in the tables is the maximum impact the film would withstand without failure.

Discussion

In recent years there has been considerable interest in improving alkyd-type resins with diisocyanates (1,5). Therefore, we prepared urethane-modified polyesteramides.

To obtain information on the reactivity of four diisocyanates with linseed isophthalic HTPA containing 10% molar excess HEFA, we studied the disappearance of isocyanate (IR band at 2270 cm^{-1}) with time (Fig. 1). Reactions were catalyzed with triethylene diamine. Nacconate 80 (mixture of tolylene-2,4- and -2,6-diisocyanate) and tolylene-2,4-diiso-

TABLE II
Air-Dried Film Properties of TDI-Modified Polyesteramides[a]

Acid or anhydride	Drier	Dry-to-touch, hr	Tack-free, hr	Rocker hardness, days aging			Chemical resistance			Impact resistance, in.-lb	
				3	10	20	5% NaOH, min	5% HCl, hr	Xylene, hr	Direct	Reverse
Linseed Polymers											
Phthalic	+	0.8	1.0	54	52	52	20	123	>192	>160	120
Isophthalic	+	0.7	0.8	56	64	60	15	166	>192	>160	>160
Endic[b]	+	0.3	0.3	60	65	70	100	110	>192	30	20
Hydrogenated endic	+	0.3	0.4	24	60	56	126	150	>192	60–80	15
Maleic	+	1.4	2.0	42	64	48	5	69	>192	>160	>160
Itaconic	+	0.8	1.3	48	61	46	20	76	>192	>160	>160
Dimer	+	20	48	4	6	8	36	76	123	>160	>160
Brassylic	+	3.1	45	6	6	4	60	45	97	>160	>160
Phthalic	—	4.3	5.0	50	55	60	9	123	>192	>160	100
Isophthalic	—	5.2	5.8	36	56	58	18	189	>192	>160	>160
Endic[b]	—	4.3	4.8	42	56	61	34	110	>192	>160	>160
Hydrogenated endic	—	11.0	19	50	60	69	21	110	>192	>160	120
Maleic	—	18	41	4	22	24	2	69	>192	>160	>160
Itaconic	—	140	140	2	2	12	6	42	144	>160	>160
Dimer	—	70	>70	6	6	8	51	69	0.1	>160	>160
Brassylic	—	>64	>64	8	10	8	15	22	>192	......	......
Soybean Polymer											
Phthalic	+	1.0	1.2	30	36	36	20	190	>224	>160	>160
Isophthalic	+	0.5	0.5	39	46	46	45	190	>224	>160	>160
Endic	+	1.2	1.5	34	38	38	20	144	0.7	>160	>160
Hydrogenated endic	+	2.3	3.0	36	42	42	225	168	167	>160	>160
Maleic	+	1.0	1.1	24	32	36	10	95	< 20	......	......
Itaconic	+	2.4	2.8	16	22	24	7	135	3	......	......
Phthalic	—	....	....	6	22	30	210	135	>224	......	......
Isophthalic	—	....	....	6	18	34	126	135	>224	......	......
Endic	—	....	....	6	14	20	180	144	0.1	>160	>160
Hydrogenated endic	—	....	....	7	14	20	1290	>218	167	>160	>160
Maleic	—	....	....	5	6	8	75	78	0	......	......
Itaconic	—	....	....	....	4	4	90	86	0	......	......

[a] Contains 10 mole per cent excess HEFA.
[b] Endic anhydride is Velsicol's designation for endo-*cis* bicyclo(2,2,1)-5-heptene-2,3-dicarboxylic anhydride.

TABLE III
Baked Film Properties of TDI-Modified Polyesteramides (200 C/10 min)

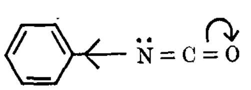
Acid or anhydride	Drier	Rocker hardness, days aging		Chemical resistance		
		3	17	5% NaOH, hr	5% HCl, hr	Xylene, hr
Linseed Polymers						
Phthalic	+	26	46	3.5	97	>192
Isophthalic	+	28	58	4.5	76	>192
Endic	+	14	37	1.0	110	>192
Hydrogenated endic	+	16	30	4.3	>171	>192
Maleic	+	18	36	0.5	69	>192
Itaconic	+	15	32	0.3	97	>192
Dimer	+	6	6	6.0	69	0.7
Brassylic	+	8	8	2.3	45	22
Phthalic	—	12	36	2.3	45	>192
Isophthalic	—	22	46	0.5	123	>192
Endic	—	10	24	0.1	110	>192
Hydrogenated endic	—	10	22	>7.0	171	>192
Maleic	—	10	20	0.1	76	>192
Itaconic	—	26	32	1.3	45	>192
Dimer	—	4	6	>7.0	53	>192
Brassylic	—	8	8	3.0	45	>192
Soybean Polymers						
Phthalic	+	14	20	38	135	>192
Isophthalic	+	23	38	23	135	>192
Endic	+	12	14	8	144	>192
Hydrogenated endic	+	12	14	69	78	>192
Maleic	+	14	18	3.8	95	>192
Itaconic	+	14	18	4.0	95	>192
Phthalic	—	12	16	12	97	>192
Isophthalic	—	20	26	7	190	>192
Endic	—	20	22	8	>218	>192
Hydrogenated endic	—	14	16	166	168	>192
Maleic	—	12	16	1.0	22	>192
Itaconic	—	8	10	2.8	97	>192

TABLE IV
Film Properties of Hexamethylene-1,6-Diisocyanate (HDI)-Modified Linseed Polyesteramides

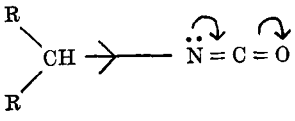
Acid or anhydride	Drier	Dry-to-touch, hr	Tack-free, hr	Rocker hardness, days aging		Chemical resistance		
				3	17	5% NaOH, hr	5% HCl, hr	Xylene, hr
Air-dried								
Maleic	+	1.3	1.4	32	44	0.1	69	>192
Maleic	—	>7	>16	25	35	0.1	69	>192
Itaconic	+	1.3	1.4	32	38	0.1	35	>192
Itaconic	—	49	70	T[a]	T	0.1	69	>192
Baked 200 C/10 Min								
Maleic	+	....	....	18	30	0.2	51	>192
Maleic	—	....	....	8	10	0.3	110	>192
Itaconic	+	....	....	8	12	0.2	45	>192
Itaconic	—	....	....	6	6	0.5	45	>192

[a] T, tacky.

cyanate (TDI) react similarly and the reaction was more than 90% complete in 6 hr. The reaction of hexamethylene 1,6-diisocyanate (HDI) with HTPA was 70% complete in 6 hr; 4,4′-methylene bis(cyclohexyl isocyanate) (HMDI) was slowest to react. After 24 hr, infrared data showed that all reactions were complete. The order of reactivity agrees with that expected based on structure. Since the mechanism involves nucleophilic attack of an alcohol (or amine) on the isocyanate carbonyl, an increase in the positive nature of the isocyanate carbonyl facilitates the reaction. Aryl isocyanates (Type I) contain an electron withdrawing group and react readily, whereas alkyl isocyanates (Type II) and particularly secondary alkyl isocyanates (e.g., HMDI) react more slowly.



Type I



Type II

This study compares the reactivity of four diisocyanates under specific reaction conditions, but not necessarily the best, for a particular isocyanate. Stannic chloride is a more effective catalyst than triethylene diamine for the HDI and HMDI reactions. At the 1 mole per cent level (based on OH content of the HTPA) of stannic chloride, the HDI and HMDI reactions are 90% complete in 1 and 3 hr, respectively. Presumably, such catalysts as di-*n*-butyltin dilaurate would be even more active (6).

Initially, linseed HTPA was prepared from 1 mole of isophthalic acid and 1.1 to 1.3 moles of HEFA followed by reaction with TDI to give urethane-polyesteramides. Effect of urethane level on properties of air-dried films with and without drier is shown in Table I. Urethane-polyesteramide films with drier had shorter drying times, improved alkali resistance, but not significantly improved hardness as the urethane content was increased. All films with drier cured rapidly to a hardness of 50 to 60 in 3 days and then increased only slightly in hardness up to 24 days. Films without drier required a longer time to become tack free (1.7–6 hr vs. 15–50 min) and generally were softer after 3 days of drying. After 24 days, the hardness of films with and without drier was similar. Impact resistance of all air-dried films was greater than 160 in.-lb. A urethane-polyesteramide (containing 30 mole per cent excess linseed HEFA) was baked at 200 C for 10 min with drier and gave a hard film with much improved alkali resistance (10 hr) compared to air-dried films (0.5 hr).

Table II lists air-dried film properties from a more extensive study of TDI-modified polyesteramides from soybean and linseed oils prepared with eight dibasic acids or anhydrides. The polyesteramides contained 10 mole per cent excess HEFA over the dibasic acid.

All linseed films with drier, except those containing dimer and brassylic acids, dried tack free in 2 hr and had 3 day Sward hardness values of 24 to 60. Films from the endic and hydrogenated endic anhydride polymers had the best drying properties of all those examined. The isophthalic acid, phthalic and endic anhydride films with drier cured almost completely in 3 days since there was little increase in hardness after this period. The maleic and itaconic films appeared to reach a maximum hardness at 10 days after which they became softer. Alkali resistance of linseed films was moderate but much improved over the corresponding unmodified polyesteramides (3,4). Resistance of linseed films to both xylene and hydrochloric acid was excellent.

Air-dried films without drier cured more slowly than films with drier, but the four best films without drier developed hardness after 20 days equivalent to or better than that of the films with drier. Hydrochloric acid and xylene resistances of the corresponding linseed films with and without drier were similar.

All air-dried soybean polymer films (Table II) with drier became tack free in 3 hr or less but were somewhat softer than the corresponding linseed films. Chemical resistance was similar to the linseed films, except the endic, maleic and itaconic polymer films had significantly poorer xylene resistance. Soybean polymer films without drier were soft at 3 days, but at 20 days those from isophthalic acid and from phthalic, endic and hydrogenated endic anhydrides had cured to moderately hard, alkali-resistant films. The hydrogenated endic film had outstanding alkali resistance.

Impact resistance of all air-dried films with and without drier was excellent except for the linseed-endic and hydrogenated endic anhydride films containing drier. These films appear to withstand direct

TABLE V
Film Properties of 4,4′-Methylene bis(cyclohexyl isocyanate) (HMDI)-Modified Soy- and Linseed-Maleic Polyesteramides

Polymer	Curing conditions	Dry-to-touch, hr	Tack-free, hr	Rocker hardness, days aging				Chemical resistance		
				3	10	17	24	5% NaOH, min	5% HCl, hr	Xylene, hr
Soybean	Baked (+)[a]	....	....	8	8	8	10	7	>167	>221
	Baked (−)	....	....	8	8	8	8	8	>167	>221
	Air (+)	< 7.5 >23	26	8	16	16	18	4	>167	< 1
	Air (−)	23	29	2[b]	2[b]	2[b]	2[b]	7	>107	2 min
Linseed	Baked (+)	....	....	22	34	40	44	39	>167	>221
	Baked (−)	....	....	10	12	16	24	17	>167	>221
	Air (+)	2.5	7	39	48	49	52	4	167	>221
	Air (−)	3.75	12	4[b]	4[b]	4[b]	6[b]	2	>167	< 1

[a] (+) = Drier, (−) = no drier.
[b] Films soft, left rocker marks.

impact better than reverse impact. The endic, hydrogenated endic and phthalic soybean films with drier have better impact resistance than the corresponding linseed materials. Films without drier may have better impact resistance than those with drier, although a more severe test is needed to clarify this point.

Baked film properties of the TDI-modified polyesteramides are shown in Table III. Data in Tables II and III reveal that the air-dried films were harder than the baked. A comparison of the six best baked linseed films (with drier) with the corresponding air-dried films showed that the baked films were much softer initially and required 2 to 3 weeks of air curing to approach the hardness of the air-dried films. Linseed polymer films that air dried soft (brassylic and dimer acid polymers) did not improve significantly in hardness when baked. Alkali resistance of the baked films was improved over the air-dried films but xylene and hydrochloric acid resistances were similar. Baked films from the soybean polymers were softer than those from the linseed products and the increase in hardness between 3 and 17 days was less for the soybean polymers.

A significant improvement in alkali resistance was observed in the baked over the air-dried soybean films. The baked phthalic and isophthalic soybean films with drier resisted alkali for 38 and 23 hr, respectively, whereas the air-dried films failed in less than 1 hr. The baked hydrogenated endic polymer films were outstanding in alkali resistance. The film without drier resisted 5% NaOH for 166 hr. As a group, the soybean films were much more resistant to alkali than the corresponding linseed films.

Isocyanate-modified coatings generally have excellent mechanical and chemical properties (1), but using aromatic diisocyanates in exterior coatings may cause film yellowing and lead to early chalking in pigmented systems (5). Part of the difficulty can be traced to the degradation of aromatic structures by ultraviolet radiation. Aliphatic diisocyanates should produce polymers with better light stability. We prepared itaconate and maleate linseed HTPA containing 10 mole per cent excess HEFA. These materials were modified with HDI to give polymers containing no aromatic rings. Their film properties are given in Table IV. Air-dried films with drier became tack free in 1.4 hr and were almost as hard as similar polymers containing TDI (Table II). Hard films were also formed from the maleic-HDI polymer when air dried without drier or baked with drier.

We also prepared the HMDI-modified linseed and soybean maleic HTPA, which contained 10 mole per cent excess HEFA. Baked and air-dried film properties are listed in Table V. Soybean films were soft and had moderate chemical resistance. Linseed films were harder than the soybean films and when made with drier attained hardness values of 44 to 52. The baked linseed film with drier was the best in this group. Impact resistance of the air-dried films from HDI and HMDI (Tables IV and V) was good to excellent, ranging from 120 to over 160 in.-lb.

Data in Table VI relate polymer film properties to the chemical linkages they contain. Polymers that

TABLE VI
Comparison of Air-Dried Film Properties of Polymers Containing Urethane Linkages[a]

Diol	Diisocyanate	Polymer linkages	Drier with (+) or without (−)	Air-dried film properties				
				Dry-to-touch, hr	Tack-free, hr	Rocker hardness	Alkali resistance	Impact resistance
HTPA	TDI	Ester, amide, urethane	+ or −	Tacky to very hard (Tables II, III)			Poor to moderate	Good to excellent
HTPA	HDI	Ester, amide, urethane	+ or −	Tacky to moderately hard (see Table IV)			Poor	Good to excellent
HTPA	HMDI	Ester, amide, urethane	+ or −	Soft to hard (see Table V)			Poor	Good to excellent
HELA	TDI	Amide, urethane	−	......	0.07	54	Excellent >10 days	Poor
HESA	TDI	Amide, urethane	−	......	0.07	63	Excellent	Poor
HELA	HDI	Amide, urethane	+ −	0.90 5.0	1.0 6.0	24 22	Excellent >10 days	Excellent
HELA	HMDI	Amide, urethane	+ −	0.05 0.03	0.07 0.03	73 70	Excellent >10 days	Fair
HESTA	TDI	Amide, urethane	−	Brittle waxy solid, mp 110 C			....	....
HELA	DDI	Amide, urethane	+ −	3 8–23	4.2	6 6	Excellent >10 days	Excellent
DA	DDI	Urethane	+	Tacky	......	....	....	....
DA	TDI	Urethane	−	0.75	0.8	4	Excellent >13 days	Excellent

[a] Abbreviations: HELA, N,N-bis(2-hydroxyethyl) linseed amide; HESA, N,N-bis(2-hydroxyethyl) soybean amide; HESTA, N,N-bis(2-hydroxyethyl) stearamide; DDI, dimer diisocyanate; DA, dimer alcohol.

contain ester, amide and urethane groups produce films that range from soft to very hard, possess good to excellent impact resistance, but lack alkali resistance. Polymer films containing amide and urethane but no ester linkages have good drying characteristics and excellent alkali resistance. Impact resistance varies from poor, for films from polymers containing TDI, to excellent for those made from HDI-modified polymers. A polymer prepared from TDI and N,N-bis(2-hydroxyethyl) stearamide is a brittle waxy solid, melting at 110 C.

An industrial company prepared a clear varnish and a white enamel (rutile titanium oxide pigment) from the TDI-modified linseed HTPA containing 10% excess HEFA. A commercial urethane-modified oil was used as a control. Formulations were brushed on cedar panels (3 coats) and exposed at Buffalo, New York, in a vertical position facing south. After 1 year the experimental varnish showed no checking, cracking, erosion, discoloration or loss of gloss. The experimental paint had better gloss retention than the control but appeared dirty. The industrial concern reported that the experimental vehicle appears to have merit as a clear varnish and gloss retentive enamel.

REFERENCES

1. Bailey, M. E., G. C. Toone and G. S. Wooster, Offic. Dig. Feder. Paint Technol. *32*, 984–1001 (1960).
2. Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 12th ed., H. A. Gardner Laboratory, Inc., Bethesda, 1962, p. 116.
3. Gast, L. E., Wilma J. Schneider and J. C. Cowan, JAOCS *43*, 418–421 (1966).
4. Gast, L. E., Wilma J. Schneider and J. C. Cowan, Ibid. *45*, 534–536 (1968).
5. Mennichen, G., J. Oil Colour Chem. Assoc. *49*, 639–647 (1966).
6. Myers, R. R., and J. S. Long, "Film Forming Compositions," Vol. 1, Marcel Dekker, Inc., New York, 1967, p. 468.

[Received November 8, 1968]