Norelac — A Proposed New Synthetic Coating Material

J. C. COWAN, A. J. LEWIS, and L. B. FALKENBURG
Bureau of Agricultural and Industrial Chemistry
Agricultural Research Administration, U. S. Department of Agriculture
Northern Regional Research Laboratory,[1] Peoria, Illinois

Introduction

The Northern Regional Research Laboratory has prepared a series of polyamides from polymeric fat acids of drying and semi-drying oils. This paper concerns the preparation and utilization of one of these polyamides, the ethylene diamine polymer of polymeric fat acids, which has been named "Norelac."[2] The other polyamides of the series will be discussed in another paper at a future date.

Norelac, a hard, transparent, resinous material, can be prepared from readily obtainable domestic oils and chemicals, since commercial production of all materials necessary for its preparation has been shown to be feasible. Little difficulty is expected in any large-scale preparation of Norelac, since small-scale preparations run very smoothly in a 15-gallon experimental varnish kettle.

Norelac is thermoplastic, is readily soluble in inexpensive solvents, and shows excellent adhesion to most surfaces, as well as excellent cohesion between its own films. These qualities, together with its water, acid, and alkali resistance, should make Norelac an interesting possibility in the protective coatings field.

Preparation of Norelac

Residual "dimeric" fat acids or esters (1) are used as the source of Norelac. By suitable polymerization of the methyl esters of soybean fat acids and subsequent distillation, the residual dimeric fat acid esters can be obtained. These residual esters actually consist of dimeric and trimeric fat acids derived from linoleic and linolenic acids present in the original oil and hereafter will be referred to as polymeric fat acids (2). The percentages of these various polymeric fractions can be readily determined with a fair degree of accuracy by the method of Cowan, Falkenburg, and Teeter (4). If desired, the free acids can be obtained by saponification of the residual esters.

Norelac is prepared by heating a mixture of approximately equivalent amounts of ethylene diamine (anhydrous or 70 percent) and the polymeric fat acids or esters. When the acids are used, foaming is encountered, but this tendency can be held to a minimum if the diamine is added slowly to the hot acids (at 150° C.). Variations in properties are obtained by using different ratios of reactants, by using different oils as a source of polymeric fat acids (giving different ratios of dimeric to trimeric fat acids), and by the degree of reaction effected in the polyamide preparation.

For protective coatings, it has been found that excellent results are obtained when equivalent amounts of reactants are used and the reaction is carried to a stage just short of gelation. A convenient method for checking the degree of reaction is either to measure the gelation time of the polyamide on a hot exposed surface (7), or to follow the amount of volatile reaction products formed during the course of the reaction. The following description gives the details of the pilot plant runs made in a 15-gallon experimental varnish kettle. This kettle is a stainless steel vessel, equipped with a turbostirrer, with electrical and steam heating units, a condenser, thermometer and thermocouple well, inlet tubes, and a connection to a mechanical vacuum pump.

A charge of 15.82 kg. of polymeric fat acids (Neutral Equivalent, 295.2) was heated to 150° C. in an atmosphere of nitrogen (carbon dioxide can also be used), and 2.30 kg. of 70-percent aqueous ethylene diamine was added slowly. The reaction proceeds with the loss of water from the aqueous diamine solution and the dehydration of the diamine salt to give amide linkages. After all the diamine was added (approximately 2 hours), the temperature was raised to 170° C. Then, over a period of 90 minutes, the pressure on the reaction mixture was reduced slowly to 13 mm. and the temperature raised to 200° C. If too rapid rise of temperature or lowering of pressure is permitted, excessive foaming may occur. The charge was held at 200° C. at 13 mm. pressure for 10 minutes, and then run into a large vat under an atmosphere of carbon dioxide. The finished product, Norelac, was allowed to cool until completely hardened. Then it was removed by inverting the vat and tapping its sides. Table I summarizes the operational details of this pilot plant preparation.

TABLE I

Record of a Pilot Plant Preparation of Norelac

Time	Temperature		Volume of distillate	Gel time at 285° C.	Remarks
	Reaction mixture	Distillate			
Minutes	*°C.*	*°C.*	*Ml.*	*Seconds*	
0	30	....	....	....	Kettle charged with acids
25	150	....	....	....	....
30	155	80	....	....	....
60	163	102	450	....	....
90	169	103	850	....	....
120	170	109	1,260	....	....
125	169	106	1,370	72	Addition of diamine completed
142	172	95	1,490	57	Pressure slowly reduced
180	202	90	....	41	370 mm. Hg.
210	197	71	....	35	93 mm. Hg.
230	200	....	....	26	13 mm. Hg.
250	201	....	1,610[1]	19	Norelac removed from kettle

[1] Theoretical amount of H_2O is 690 ml. from ethylene diamine solution plus 966 ml. from reaction = 1,656 ml.

Two samples of the product were placed in reaction vessels and heated at 215° C., with stirring of the fused product. One was fused under nitrogen and the

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[1] The Northern Regional Research Laboratory is one of four Regional Laboratories authorized by Congress in the Agricultural Research Act of 1938 for the purpose of conducting research to develop new uses and outlets for agricultural commodities. These Laboratories are operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] From *NO*rthern *RE*gional *LAC*quer.

TABLE II

Norelac Samples from Different Preparations

Norelac number	Source of polymeric acids	Mole percent dimeric fat acids	Equivalent ratio amine/acids	Neutralization equivalent		Melting range — °C.
				Carboxylic acid	Base	
1	Soybean	73	1/1	3,000	4,140	96-102
2	Soybean	73	1/0.8	7,800	1,490	85-92
3	Linseed (esters)	45	1.1/1	......	......	94-99
4	Soybean[1]	73	1/1	3,600	5,500	108-112
5	Sample taken 40 minutes before completion of reaction	73	1/1	3,150	5,150	103-107
6	Sample taken 125 minutes before completion of reaction	73	1/1	1,800	2,150	89-93

[1] Commercial dimeric fat acids. Samples 4, 5, and 6 are representative samples taken from the preparation shown in Table I.

other under carbon dioxide. Neither gelled within six hours.

Variations in properties of different Norelac preparations are shown in Table II.

Properties of Norelac

Solubility. Since most surface coatings are applied in liquid form, a knowledge of the solubility characteristics of Norelac is essential for its proper use in the coating field. One of the unusual properties of this polyamide is its solubility in organic solvents. When properly prepared, Norelac is soluble in alcohols, amines, fatty acids, some high aldehydes and ketones, and in a few halogenated hydrocarbons. It is insoluble, or only very slightly soluble, in hydrocarbons, esters, glycols, nitroparaffins, and most halogenated hydrocarbons. Secondary solvents include the aliphatic and aromatic hydrocarbons and their halogenated derivatives. Solutions of Norelac in butyl and isopropyl alcohol have high dilution ratios with these secondary solvents, but most non-solvents precipitate Norelac from its solutions with single solvents. However, if Norelac is dissolved in a combination of primary and secondary solvents, a diluent may be added in some quantity before precipitation occurs.

Solubilities were usually determined by placing 1 g. of Norelac and 10 ml. of solvent in a test tube and shaking vigorously for 10 hours. If the Norelac was not dissolved, the tube was warmed in a bath of boiling water and the effect was noted. This method was convenient, but it was soon noticed that some mixtures gave two liquid phases when the solid-liquid ratio was about 1 to 10. At higher solid-liquid ratios of 3 or 4 to 10, the phases disappeared giving free flowing solutions. At still higher solid-liquid ratios, 5 or 6 to 10, the Norelac dissolved on heating, but the solution gelled on cooling to room temperature. For example, when a particular Norelac sample was added to isopropyl alcohol the mixture gave two phases when it contained less than 30 percent solid; showed complete solubility at room temperature when the solution contained 30-35 percent solids; and showed complete solubility at boiling temperatures when the solution contained 35-60 percent solids with gels forming on cooling. The solubility data for Norelac with single solvents are summarized in Table III.

Table IV gives dilution ratios for Norelac which were determined in butyl and isopropyl alcohol solutions, using the method of Brown and Bogin (3). A definite volume of Norelac solution was placed in a test tube and titrated with diluent until a cloudy solution or precipitate formed. The dilution ratios of various concentrations of Norelac in butyl and isopropyl alcohol with V.M.P. naphtha and lacquer diluent were determined to illustrate the effect of concentration of Norelac on the ratios. Figure 1 shows the effect of Norelac concentration on dilution ratios.

TABLE IV

Dilution Ratios for Norelac[1]

Norelac weight	Solvent	Diluent	Dilution ratio
Percent			
30	Isopropyl alcohol	V.M.P. naphtha	7.0
30	n-Butyl alcohol	V.M.P. naphtha	7.7
50	n-Butyl alcohol	V.M.P. naphtha	5.4
30	n-Butyl alcohol	Lacquer diluent	7.6
50	n-Butyl alcohol	Toluene	>20.0
30	n-Butyl alcohol	Hexyl chloride	>20.0
30	n-Butyl alcohol	Trichloroethylene	>20.0
30	n-Butyl alcohol	Carbon tetrachloride	>20.0
30	n-Butyl alcohol	Chlorobenzene	>18.0
30	n-Butyl alcohol	Methylene chloride	7.7
30	n-Butyl alcohol	Ethylene chloride	4.3
30	n-Butyl alcohol	Methanol	0.6
30	n-Butyl alcohol	Ethanol	0.9
30	n-Butyl alcohol	Ethyl acetate	0.9
30	n-Butyl alcohol	n-Butyl acetate	2.0
30	n-Butyl alcohol	Amyl acetate	3.1
30	n-Butyl alcohol	Acetone	0.5
30	n-Butyl alcohol	Methyl cellosolve	0.9
30	n-Butyl alcohol	Nitroethane	0.3

[1] Norelac 1 (Table II) used in determining these ratios.

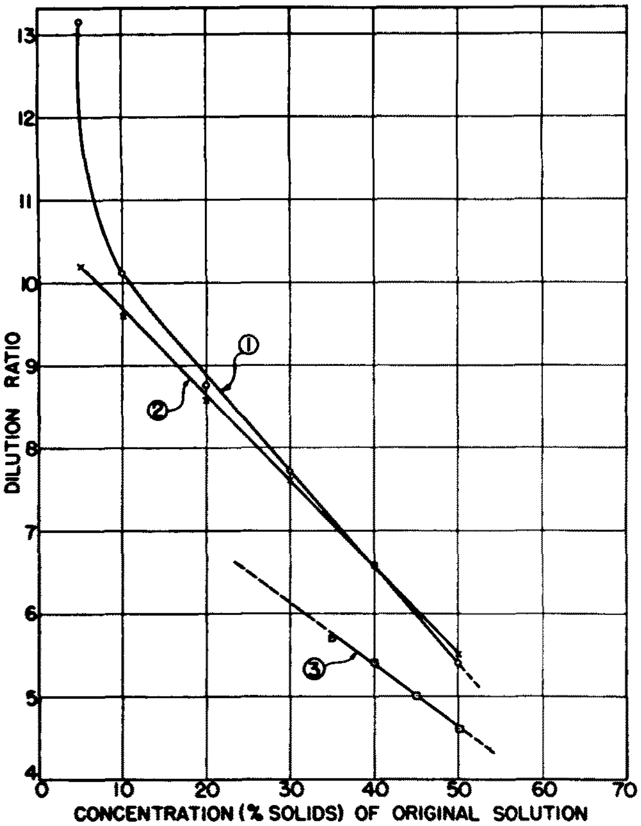

FIG. 1. Dilution Ratios of Norelac 1 in n-Butyl and Isopropyl Alcohols:

1) Solvent, n-butyl alcohol; Diluent, V.M.P. naphtha
2) Solvent, n-butyl alcohol; Diluent, lacquer diluent.
3) Solvent, isopropyl alcohol; Diluent, lacquer diluent.

TABLE III

Effect of Organic Solvents on Norelac

Solvent	Solubility [1] At 25° C.	Solubility [1] At 100° C.[2]	Remarks
Hydrocarbons and chloro derivatives:			
V.M.P. Naphtha	Insoluble	Insoluble	Softened
Lacquer diluent [3]	Insoluble	Insoluble	Unchanged
Benzene	Insoluble	Very slightly soluble	Swelled
Toluene	Insoluble	Very slightly soluble	Swelled
Xylene	Insoluble	Very slightly soluble	Swelled
Decalin	Insoluble	Insoluble	Softened
Cyclohexane	Insoluble	Very slightly soluble	Softened
Turpentine	Very slightly soluble	Very slightly soluble	Swelled
Indene	Very slightly soluble	Very slightly soluble	Swelled
Chloroform	Soluble	Soluble	....
Carbon tetrachloride	Insoluble	Two liquid phases	Liquefied
Chlorobenzene	Insoluble	Two liquid phases	Swelled
[illegible]	Slightly soluble	Soluble	Liquefied
[illegible]	[illegible]	Slightly soluble	Softened
[illegible]	[illegible]	Solubility increased	Liquefied
Hexyl chloride	Slightly soluble	Soluble	Gelled on cooling
Esters and ethers:			
Diethyl ether	Insoluble	Insoluble	....
β, β′-dichloroethyl ether	Insoluble	Insoluble	Softened at 25° C.
Ethyl acetate	Very slightly soluble	Slightly soluble	....
Ethyl lactate	Slightly soluble	Slightly soluble	Softened
Ethyl malonate	Insoluble	Insoluble	....
Amyl acetate	Very slightly soluble	Slightly soluble	Two phases formed; gelled on cooling
n-Butyl acetate	Very slightly soluble	Slightly soluble	Two phases formed; gelled on cooling
Methyl stearate	Very slightly soluble	Very slightly soluble	....
n-Butyl stearate	Very slightly soluble	Very slightly soluble	....
Methyl oleate	Very slightly soluble	Very slightly soluble	....
n-Butyl oleate	Very slightly soluble	Very slightly soluble	....
Tributyl citrate	Insoluble	Insoluble	....
n-Butyl phthalate	Insoluble	Insoluble	....
Triethyl phosphate	Very slightly soluble	Very slightly soluble	....
Tributyl phosphate	Slightly soluble	Soluble	Gelled on cooling
Soybean oil	Insoluble	Insoluble	....
Ethylene glycol diacetate	Insoluble	Insoluble	....
Methyl cellosolve	Insoluble	Very slightly soluble	....
Benzyl cellosolve	Insoluble	Soluble	Two phases formed on cooling
Methyl carbitol	Insoluble	Very slightly soluble	....
Aldehydes and Ketones:			
Diacetone alcohol	Very slightly soluble	Slightly soluble	Softened
Acetonyl acetone	Very slightly soluble	Very slightly soluble	....
Acetone	Insoluble	Very slightly soluble	Softened slightly
Methyl ethyl ketone	Insoluble	Very slightly soluble	Softened slightly
Methyl amyl ketone	Very slightly soluble	Very slightly soluble	Softened slightly
Cyclohexanone	Slightly soluble	Soluble	Gelled on cooling
Isophorone	Slightly soluble	Soluble	Thixotropic gel on cooling
Mesityl oxide	Soluble	....	....
n-Butyl aldehyde	Very slightly soluble	Slightly soluble	....
Heptaldehyde	Slightly soluble	Soluble	Gelled on cooling
Benzaldehyde	Slightly soluble	Soluble	Precipitated on cooling
Alcohols:			
Methyl alcohol [4]	Very slightly soluble	Two liquid phases	Two phases formed on heating
Ethyl alcohol (95%)	Very slightly soluble	Two liquid phases	....
Ethyl alcohol (abs.)	Slightly soluble	Two liquid phases	....
Isopropyl alcohol	Soluble	Two liquid phases	....
sec-Butyl alcohol	Soluble	....	....
iso-Butyl alcohol	Soluble	....	....
Tetrahydrofurfuryl alcohol	Soluble	....	....
Cyclohexanol	Soluble	....	....
tert-Amyl alcohol	Soluble	....	....
Capryl alcohol	Soluble	....	....
Chlorohydrin	Two liquid phases	Soluble	....
Nitro Derivatives of Hydrocarbons:			
Nitromethane	Insoluble	Insoluble	....
Nitroethane	Insoluble	Very slightly soluble	....
1-Nitropropane	Insoluble	Very slightly soluble	....
2-Nitropropane	Insoluble	Very slightly soluble	....
1-Chloro, 1-nitro-propane	Very slightly soluble	Slightly soluble	....
Nitrobenzene	Very slightly soluble	Soluble	Softened at 25° C.
Nitriles and Amides:			
Amyl nitrile	Insoluble	Insoluble	....
Dimethyl formamide	Very slightly soluble	Two liquid phases	Softened at 25° C.
N, N-diethyl lauramide	Slightly soluble	Soluble	Gelled on cooling
Amines:			
n-Butyl amine	Soluble	....	....
Piperidine	Soluble	....	....
Pyridine	Soluble	....	....
Diethyl amine	Soluble	....	....
Ethylene diamine	Insoluble	Insoluble	....
Di-n-Butyl amine	Very slightly soluble	Soluble	Softened at 25° C.
Tri-n-Butyl amine	Insoluble	Insoluble	....
Aniline	Slightly soluble	Soluble	Gelled on cooling
Dimethyl aniline	Very slightly soluble	Slightly soluble	Softened at 25° C.
Polyhydric Alcohols:			
Ethylene glycol	Insoluble	Insoluble	....
Glycerol	Insoluble	Insoluble	....
Trimethylene glycol	Insoluble	Insoluble	....
Diethylene glycol	Insoluble	Insoluble	....
Ethanolamine	Insoluble	Insoluble	....
Monoisopropanol amine	Insoluble	Insoluble	....
2-Amino, 1-Butanol	Insoluble	Insoluble	....
2-Nitro, 1-Butanol	Slightly soluble	Slightly soluble	....
1,5-Pentandiol	Insoluble	Insoluble	....
Acids:			
Acetic acid	Slightly soluble	Soluble	Separated on cooling
n-Butyric acid	Soluble	Soluble	....
Caproic acid	Soluble	....	....
Linseed fatty acids	Soluble	....	....
Soybean fatty acids	Soluble	....	....
Polymeric fat acids	Soluble (when heated to 150° C.)	....	....
Lactic acid	Insoluble	Very slightly soluble	....

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[1] Solubilities of Norelac from the same residual dimeric fat acids vary somewhat with the degree of polymerization.

[2] Solubility at 100° C. or at approximately the boiling point of the solvent.

[3] B.P. 69-96° C.

[4] With lower alcohols two liquid phases are formed when the ratio of solid to liquid is very low. If the ratio is increased sufficiently, complete solubility results except with methanol and 95 percent ethyl alcohol but only over a limited range.

The change in viscosity with solid content is important in lacquer or varnish formulation. Hence, the viscosities of various concentrations of Norelac in butyl alcohol were determined. Figure 2 shows the viscosities obtained using Gardner-Holdt viscosity tubes. To illustrate the effect of a secondary solvent on flow characteristics of Norelac solutions, the viscosities were determined at different dilution ratios. Figures 3 and 4 show the change in viscosity of 35 percent Norelac solutions with different solvent ratios.

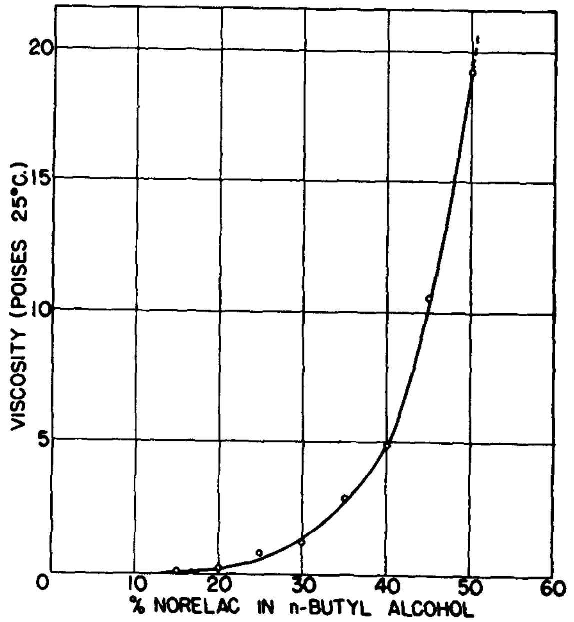


FIG. 2. Viscosity of Norelac 1 in n-Butyl Alcohol Solutions.

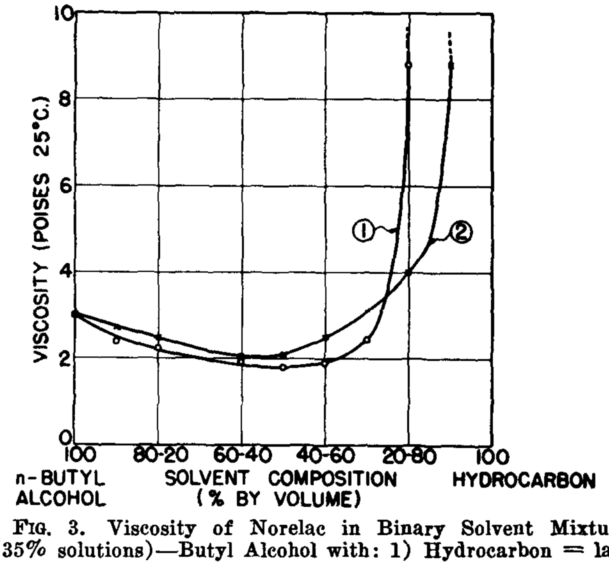


FIG. 3. Viscosity of Norelac in Binary Solvent Mixture (35% solutions)—Butyl Alcohol with: 1) Hydrocarbon = lacquer diluent; 2) Hydrocarbon = toluene.

Compatibility With Resins. Since many lacquer formulations are improved by the addition of a second and sometimes a third resin, the compatibility of Norelac with other resins was determined. Equal weights of Norelac and resin were dissolved in a mixture of equal volumes of butyl alcohol and toluene. When the resin was insoluble in butyl alcohol-toluene mixture, a third solvent was added to dissolve it. For example, one part nitrocellulose and three parts Norelac were dissolved to give a 30 percent solution in a toluene, butyl alcohol and amyl acetate solvent mixture (equal parts by volume). If the resulting solutions were clear, films were cast and the appearances of the films were noted. Table V shows the results of these tests.

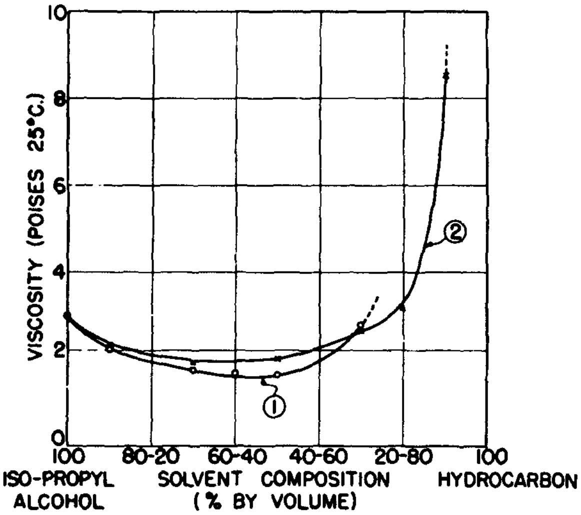


FIG. 4. Viscosity of Norelac 1 in Binary Solvent Mixture (35% solutions)—Isopropyl Alcohol with: 1) Hydrocarbon = lacquer diluent; 2) Hydrocarbon = toluene.

TABLE V

Compatibility of Norelac with Resins: 1-1 Ratio of Norelac[1] to Resin

Resin	Solubility—Butyl alcohol-toluene 30% solution in equal parts	Appearance of film[2]
Amberol ST-137	Miscible	Clear
Manila	Miscible	Clear
Piccolyte	Miscible	Cloudy
Bakelite BR-254	Miscible	Clear
Kauri	Miscible	Clear
Vinsol	Miscible	Clear
Coumarone-Indene, M.P. 115-130° C.	Immiscible	....
Nevillac, M.P. 85-95° C.	Miscible	Clear
Rosin	Miscible	Clear
Ester gum	Miscible	Clear
Amberol B/S-1	Miscible	Hazy
Amberol 801	Miscible	Hazy
Batu	Two phases	....
Falkote 285	Miscible	Slightly hazy
Falkote 240	Miscible	Slightly hazy
Gilsonite	Immiscible	....
Amberol M-16	Miscible	Slightly hazy
Amberol K-12A	Miscible	Clear
Amberol 400	Miscible	Cloudy
Nitrocellulose	Miscible[3]	Clear
Ethylcellulose	Two phases[4]	....

[1] Norelac 1 (Table II) used in determining these compatibilities.

[2] It is quite possible that different ratios of resin to Norelac might give clear films. Also cloudy films may be a result of incorrect solvent balance.

[3] Three parts Norelac to 1 of nitrocellulose (Solvent: equal parts of butyl alcohol, toluene, and amyl acetate).

[4] Solvent was butyl alcohol.

Film Evaluation. Since Norelac is a new material, it was necessary to make comparisons with other protective coatings now in use. Tests reported here are only preliminary in nature, and a more comprehensive report on the characteristics of Norelac as a coating will be made later. Comparisons were made directly with nitrocellulose (R.S., ¼ sec.), standard ethyl cellulose (48.5-49.5 ethoxyl content), orange shellac, and a damar varnish.

Norelac was dissolved in isopropyl alcohol and V.M.P. naphtha solvent mixture (equal parts by volume), nitrocellulose in butyl acetate-V.M.P. naphtha mixture, and ethylcellulose in isopropyl alcohol. The orange shellac, a commercial "4-pound cut," and the damar varnish, a commercial preparation containing approximately 50 percent of resin in equal parts of mineral spirits and turpentine, were used as received.

Drying times of Norelac solutions and other simple lacquers and spirit varnishes are compared in Table VI. A Sanderson Drying Meter (8), operating at a temperature of 77° F. and 50 ± 2 percent relative humidity was used. Resistance of the same films to cold and hot water, dilute and concentrated alkali, dilute acetic acid, and concentrated sulfuric acids are reported in Table VII. The films used in the cold and hot water tests were prepared by flo-coating tinplate panels with the solutions. The other tests were made on films deposited on test tubes by dipping in solutions, inverting, and allowing to air-dry for five days at 77° F. and 50 ± 2 percent relative humidity.

TABLE VI

Drying Times on Sanderson Drying Meter

Material	Set-to-touch [1]	Free-from-tack [2]
	Minutes	
Nitrocellulose (30% solids)	2	5 min.
Ethylcellulose (30% solids)	2	2 min.
Norelac 4 (30% solids)	2	16½ hrs.
Norelac 1 (30% solids)	5	68 hrs.
Orange shellac	5	Over 14 days
Damar varnish	5	96 hrs.

[1] The period of time required for the film to dry on glass plate to such a degree that sand does not adhere to the film on vigorous brushing.

[2] The period of time required for the film to dry to such a degree that sand does not adhere to the film on inversion of glass plate and striking of plate sharply with brush handle.

A film of Norelac No. 4 (Table II) was deposited on a glass plate from solution, using a 0.003 inch doctor blade. A definite area was marked off, and the excess film removed. The weight of the film was determined by difference, and the thickness was determined with an Ames gauge. The film density of Norelac was approximately 0.95 g./cc. On this basis, one pound of Norelac would cover 29,100 square inches with a film 0.001-inch thick.

The flexibility of Norelac was tested by flo-coating three 3- x 5-inch tin plate panels with a 30 percent solution, allowing the film to air-dry for seven days, and then bending the panels over a 0.125 inch mandrel. On inspection with a low-power magnifying lens, it was noted that there was no cracking, checking, or spalling off of the Norelac film.

The adhesion to tin, steel, and glass surfaces was qualitatively tested by the thumbnail method. Surfaces were flo-coated on 3- x 5-inch panels, and the films were allowed to air-dry for seven days. An attempt was made to remove the film from the surface by exerting maximum pressure with the thumbnail while it was moved across the film. Excellent adhesion was obtained on tin, steel, and glass. In addition, strips of wood, paper, glassine, cellophane, lead foil, and tin were laminated with Norelac by means of heat and pressure. The strips were strongly bonded to-

TABLE VII

Comparative Tests on Films of Norelac, Ethylcellulose, Nitrocellulose, Orange Shellac and Damar Varnish

Film-forming material and percentage solids in solution	Condition of film after immersion in—						Sward hardness. (Plate glass = 100)
	Cold water	Hot water	4% acetic acid	5% sodium hydroxide	20% sodium hydroxide	75% sulphuric acid	
Ethylcellulose—10%	4 days—Very slightly cloudy	5 minutes—Badly whitened; film loosened	4 days—Very slightly cloudy	3 days—Very white and cloudy	3 days—Moderately whitened and blurred	3 hours—Entirely decomposed	72
Ethylcellulose—30%	7 days—Cloudy	5 minutes—Whitened	15 days—Unaffected	7 days—Unaffected	8 days—Unaffected	3 hours—Whitened and blistered; after 18 hours partially decomposed	....
Nitrocellulose—15%	4 days—Unaffected	5 minutes—Slightly cloudy	40 hours—Entire film off in sheets	24 hours—Completely dissolved	5 hours—Completely dissolved	3 hours—Badly checked and scaled off on finger	60
Nitrocellulose—30%	7 days—Unaffected but loosened from plate	15 minutes—Whitened; film off when dried	2 days—Film off	18 hours—Dissolved	18 hours—Dissolved	30 minutes—Badly checked and scaled off on finger	....
Norelac 1[1]—30%	4-days—Very slightly cloudy	5 minutes—Softened	4 days—Whitened and wrinkled	3 days—Unaffected	3 days—Unaffected	3 days—Discolored but otherwise unaffected	26 [2]
Norelac 2[1]—35%	4 days—Cloudy	5 minutes—Softened	17 hours—Loosened and wrinkled	3 days—Unaffected	3 days—Unaffected	3 days—Discolored, but otherwise unaffected	....
Norelac 4[1]—30%	7 days—Unaffected	5 minutes—White; after 15 minutes, softened	15 days—Unaffected	7 days—Unaffected	8 days—Unaffected	7 days—Discolored. but otherwise unaffected	30
Norelac 4—15%	7 days—Unaffected	5 minutes—Whitened; after 15 minutes, white and considerably pitted	15 days—Unaffected	7 days—Unaffected	14 days—Unaffected	7 days—Discolored, but otherwise unaffected	....
Norelac 4—10%	7 days—Unaffected	5 minutes—Whitened; after 15 minutes, whitened; moderately pitted	15 days—Unaffected	7 days—Unaffected	14 days—Unaffected	7 days—Discolored, but otherwise unaffected	....
Orange shellac	2 days—Badly whitened	5 minutes—Film off	2 days—Moderately whitened	45 minutes—Dissolved	1 hour—Dissolved	1 hour—Wrinkled and partially dissolved	32
Damar varnish	2 days—Whitened	3 minutes—Film off	2 days—Badly whitened; pinholed	16 hours—Whitened	16 hours—Whitened	Discoloration with surface cracks	31

[1] See Table II.

[2] Hardness value for 1 part Norelac 1 plus 1 part Kauri = 58. Hardness value for 1 part Norelac 1 plus 1 part Ester gum = 53. Hardness value for 1 part Norelac 1 plus 1 part Amberol K-12A = 65.

gether, showing that Norelac may find use as a heat-sealing and laminating agent. Further work on the adaptation of Norelac to these uses is now in progress.

A number of outdoor exposures and other types of tests are also in progress, and the results will be published when completed. Clear Norelac films brushed on maple panels in three coats have been found to have excellent durability during an outdoor exposure test of six months at an angle of 45 degrees facing south at Peoria, Illinois. In this test, the films compared very favorably with butyl methacrylate films which were exposed at the same time. Also, clear films of nitrocellulose, butyl methacrylate, and Norelac were exposed in a National Accelerated Weathering Unit for 1,090 hours. Table VIII shows the results of these exposures. A large number of clear and pigmented Norelac coatings applied by spraying are being tested.

TABLE VIII

Condition of Films After Exposure in Weathering Unit

Time of exposure (hours)	Norelac 1 (Table II)	Butyl methacrylate	Nitrocellulose
108	Good	Good—film slightly pitted	Good
164	Dull finish, but in good condition	Slightly pitted	Cloudy; film surface powdery
566	Dull finish, but in good condition	Badly pitted	Complete failure; film destroyed
1,090	Film intact, but somewhat dull; no cracks or pits	Very badly pitted	....

In connection with the durability of Norelac, it is interesting to note that its film converts to an insoluble state. This conversion is slow. For example, a film exposed for one month was still somewhat soluble in butanol, but after four months it was insoluble. Methods of accelerating this conversion are being investigated.

Discussion of Results

An examination of Table VII gives a clear indication of the properties of Norelac films as compared with some other films. Norelac is equal or superior to unmodified ethylcellulose, nitrocellulose, orange shellac and damar varnish in resistance to cold water, 4 percent acetic acid, 5 and 20 percent sodium hydroxide, and 75 percent sulfuric acid. Norelac is inferior to ethylcellulose and nitrocellulose, and nearly equal or superior to damar varnish and orange shellac in hardness and resistance to hot water.

These properties alone would be sufficient to warrant more extensive work on Norelac, but other properties make it even more attractive. Norelac is thermoplastic, and may be useful as a heat-sealing, moistureproofing, and laminating agent for paper, wood, cellophane, and other materials. Its compatibility with resins shows that a wide range of materials may be used to modify Norelac to give a large number of possible compositions. It has rather unusual solubilities, which will be discussed later, but inexpensive solvent combinations suitable for spraying, brushing, and dipping can be obtained. Norelac has excellent properties, almost immediately after application, which might shorten some production schedules. Also, it has functionality which can convert the film by reaction with oxygen to form an insoluble, three-dimensional polymer. Although this conversion is slow, some means of accelerating it may be discovered after further investigation.

The two properties which may limit the use of Norelac as a protective coating are the relative softness of its films and its low melting point. These properties restrict its use where very hard films and resistance to hot water are necessary. However, in its present stage of development, Norelac is a superior material for use where these two factors are not important. Its use as a spirit varnish to replace shellac and to protect many surfaces from exposure to weathering and corrosive solutions appears feasible. For example, it merits consideration as an undercoating in place of shellac where good adhesion and sealing qualities are needed and in the protection of exposed surfaces on automobiles, aircraft, etc. where good durability and elasticity are desirable. Its alkali and acid resistance indicate that it could be used to protect surfaces exposed to dilute or moderately concentrated solutions of alkalies or acids as well as those exposed to soap solutions.

Both reactants needed for Norelac have been prepared on a large-scale industrial basis. Ethylene diamine needs no description, since it has been widely advertised by a large chemical company. The polymeric fat acids have been produced by companies specializing in the bodying of oils and distillation of fat acids. During the past year, production was achieved in existing equipment, and if raw material is allocated for the purpose, polymeric fat acids can be made available for this new use. The production of Norelac from these reactants on a pilot plant scale presented but few difficulties. Preparation of Norelac from soybean polymeric fat acids was particularly free from operational difficulties. By the simple expedient of adding the diamine to the hot acids under an inert atmosphere, foaming and conversion to three-dimensional polymers were controlled. There is danger of gelation during the preparation of Norelac, but samples of soybean Norelac described in the pilot plant run failed to gel within six hours at 215° C. under inert atmosphere. Six hours is ample time to empty most large esterification kettles. The possibility that Norelac may gel after flowing from the kettle must also be considered. Special trays or tubs might be necessary, but it is believed that little difficulty will be encountered on large-scale operation.

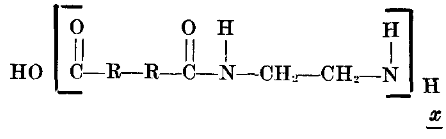
As was shown in Table II, variations in Norelac can be obtained by the use of different oils as a source of the polymeric fat acids, by the degree of condensation effected, and by the ratio of reactants used. The differences between various batches made from different oils is directly traceable in part to the composition of the polymeric fat acids . The ratio of dimeric to trimeric fat acids present varies considerably with the oil used. For example, linseed oil gives a dimeric/trimeric ratio of 0.8 to 1, while soybean oil gives 1.5 to 1 under comparable operating conditions (4). A higher trimeric acid content reduces the degree of reaction which it is possible to obtain before gelation occurs (5). Also, the degree of reaction of the condensation of polymeric fat acids with ethylene diamine will affect the properties of the product. For example, films from Norelac No. 1 (Table II) are wrinkled after exposure to 4 percent acetic acid, while films from Norelac No. 4 are not. The main difference between these samples of Norelac is the degree of condensation effected in their preparation. In addition, the polymeric fat acids obtained from soybean oil have different physical properties and contain less unsaturation than polymeric fat acids from linseed oil (1). Consequently, Norelac from linseed oil contains more functional groups and its films would become three-dimensional and insoluble at a more rapid rate than films from soybean Norelac. However, both soybean and linseed Norelac give films which set-to-touch rapidly and dry almost free from tack in a few minutes.

If the polyamide formation is carried too far, gelation occurs with formation of three-dimensional polymers. The gel is insoluble and infusible, and consequently has no utility as a surface coating. If the reaction is not carried far enough, the product is soft and gives relatively inferior films.

The solubility of Norelac is unusual enough to arouse some speculation as to the behavior of different solvents. Organic liquids which contain electron-acceptor groups, such as alcohols, amines, and acids, are primary solvents for Norelac. Apparently, compounds must contain about three to four carbon atoms and an electron-acceptor group in order to act as solvents. Chloroform is an exception, as regards the number of carbon atoms, but here the chlorine aids in the dissolution; also, chloroform has been shown to contain the electron-acceptor group (9). Supporting evidence on the solubilizing effect of chlorine is found in high dilution ratios with chlorohydrocarbons. For example, in Table IV, compare methylene chloride with carbon tetrachloride; also, lacquer diluent with hexyl chloride. If the electron-accepting capacity of the molecule is too great, the solubility is reduced. For example, amyl alcohol is a primary solvent for Norelac, but 1, 5-pentandiol is not. The correct balance of electron-accepting power and hydrocarbon solubilizing ability must be maintained to dissolve or maintain Norelac in solution.

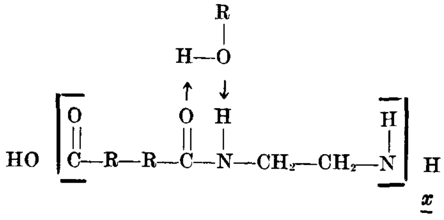
Figures 3 and 4 show that 35 percent Norelac solutions in butyl alcohol-toluene, and in isopropyl alcohol-toluene, will gel at approximately 10 percent alcohol content. These data are supporting proof for the formation of hydrogen bridges in solvation of Norelac. Norelac may have a structure similar to that shown in Formula I in which no provision is made for trimeric fat acid.

Let us assume that the alcohol forms a cyclic structure with amide linkages, as shown in Formula II.



$$\mathrm{HO}\left[\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\mathrm{R}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{N}}\right]_{x}\mathrm{H}$$

Norelac—Formula I



$$\mathrm{HO}\left[\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\mathrm{R}-\overset{\overset{\displaystyle \overset{\displaystyle \mathrm{H}-\overset{\displaystyle \mathrm{R}}{\overset{|}{\mathrm{O}}}}{\uparrow\ \ \downarrow}}{\mathrm{O}\ \ \mathrm{H}}}{\overset{\|\ \ \ \ |}{\mathrm{C}-\mathrm{N}}}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{N}}\right]_{x}\mathrm{H}$$

Norelac—Formula II (showing one bonded alcohol)

Then, for every amide group, one equivalent of alcohol will be necessary for any given linkage to be soluble in the second solvent, such as toluene. It may be fortuitous, but the concentration of butyl and isopropyl alcohol necessary to maintain solution of Norelac in toluene is approximately equivalent to the potential amide groupings. Each polymeric linkage in Formula I contains two potential amide groups and has a molecular weight of 584 (equivalent weight of 292). Each linkage should require two equivalents of alcohol for solvation. At a 10 percent concentration, or 0.09 equivalent of butyl alcohol or 0.11 equivalent of isopropyl alcohol, gelation occurs in 0.12 equivalent solution of Norelac.

In addition, the viscosities of the isopropyl alcohol-toluene and butyl alcohol-toluene solutions undergo rapid change when the concentration of alcohol drops below 20 percent. If, as shown in Formula II, the alcohol forms a cyclic structure with amide linkages, the nitrogen atom still retains electrons which can bridge with hydrogen. Twenty-percent concentration corresponds to 0.22 equivalent of isopropyl alcohol, 0.18 equivalent of butyl alcohol, and 0.24 equivalent of electron-donor groups. The shape of the viscosity curve is indicative of an enormous change in solubility behavior, and the suggested solvation action of alcohol appears to be a satisfactory explanation. The slight difference in effect between isopropyl and butyl alcohol is most likely caused by the more hydrocarbon-like nature of butyl alcohol. The gelation of Norelac may be considered to be imminent when the concentration of the alcohol drops below one equivalent per amide group. The gelation actually occurs when a few amide linkages in polymeric molecules are freed of alcohol of solvation. With hydrocarbons which do not have high dilution rates, the Norelac formed gels at approximately 20 percent alcohol content, or two equivalents per amide linkage. This gelation is also supporting evidence for the solvation of Norelac by alcohols.

Summary

A new protective coating material, Norelac, the ethylene diamine polyamide of polymeric fat acids has been described. A preliminary report on its properties indicates that it may prove to be a superior protective coating for wood, metal, and other materials, and an adhesive for heat-sealing and laminating of paper, cellophane, glassine, and other packaging materials. The solubility characteristics of Norelac show that solvation probably occurs in compounds containing electron-acceptor groups, such as alcohols, amines, acids, and chloroform.

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