End-Use Evaluation of Some Copolymers and Terpolymers of Vinyl Ethers of Linseed Conjugated Fatty Alcohols[1]

R. H. DENT and B. G. BRAND, Battelle Memorial Institute, Columbus, Ohio, and
H. M. TEETER and J. C. COWAN, Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Copolymers and terpolymers, based on vinyl ethers from linseed conjugated fatty alcohols and selected as having the most potential for commercial use, were evaluated as chemically resistant coatings, metal-decorating coatings, small-appliance and architectural finishes, wire coatings, and adhesives. Studies show these materials to have promise in areas where a high-temperature baking schedule can be tolerated and where color is not of prime importance. Good compatibility with most commonly used pigments was observed. As wire coatings, film showed good continuity and had superior dielectric strength and resistance to cut-through; however, improvement in flexibility and adhesion to copper would be needed for successful application. Performance as adhesives was disappointing, since curing in the absence of air was poor. The polymers showed some promise as can coatings, but the need for modifications in them was demonstrated.

Introduction

As a result of an integral part of a program on the research and development of vinyl ethers from unsaturated fatty alcohols, the Northern Regional Research Laboratory contracted with Battelle Memorial Institute to evaluate the potential of polymers and copolymers of these vinyl ethers in protective coatings (2,4,5,8,10). After limited evaluation tests at the Northern Laboratory, Battelle initially examined eight selected samples. Results indicated that substantial improvement was needed before the vinyl ether films would meet all requirements, but that terpolymers made with allyl vinyl ether were promising (4). Because allyl vinyl ether readily undergoes a rearrangement on heating, extensive developmental work with this terpolymer seemed unadvisable.

As a result of periodic research conferences, cooperation with industrial companies (1), and progressive improvement in the quality of films prepared from copolymers, five samples were selected from more than 300 polymeric derivatives for end-use evaluation: The names of these five selected polymers, and the code by which to identify them, are found in Table I and their film properties in Table II.

TABLE I

Copolymers Selected for End-Use Evaluation

Polymer	Code
Isobutyl(3)conjugated soybean(1)vinyl ether [a]	IB(3)CS(1)[a]
Cyclopentadiene (1.4) conjugated soybean (1)vinyl ether	CP(1.4)CS(1)
Cyclopentadiene(1.5)conjugated linseed (1)vinyl ether	CP(1.5)CL(1)
Dicyclopentadienyl(3)conjugated linseed vinyl ether	DCP(3)CL(1)
Cyclopentadinene(2.6)isobutyl(1)conjugated linseed(1)vinyl ether	CP(2.6) IB(1)CL(1)

[a] Numerals indicate moles of vinyl ethers or other monomer incorporated into polymer.

Data

IB(3)CS(1) polymer represented the first samples evaluated in our studies (2,4,5,8,10) and serves as a guidepost to show improvements or changes in properties. The other polymers selected were prepared with cyclic monomers, such as cyclopentadiene or dicyclopentadienyl vinyl ether. The information on how to prepare these polymers is published elsewhere (3). Further improvements in polymer properties have been achieved by styrenation; this work is also published elsewhere (7). Cyclic monomers copolymerized with fatty vinyl ethers give polymers that air-dry and bake to clear, nontacky films clearly superior to previously prepared films of vinyl ether polymers including polymers containing allyl vinyl ether (4). Caustic resistance, xylene resistance, and Sward hardness of films from polymers of cyclic vinyl ether copolymers are much better than films from the IB(3)CS(1) polymer. Flexibility and adhesion are not as good, but abrasion resistance is substantially better.

TABLE II

Some Properties of Clear and Pigmented Vinyl Ether Films Baked at 450F for 15 min. Driers were 0.01% cobalt and 0.5% lead naphthenate eclculated as metal ion content based on resin nonvolatile for both clear and pigmented (30% TiO_2) films.

Polymer film	Sward Hardness [a]		Impact Resistance in ft–lb	Caustic Resistance [b] in hr	Xylene Resistance in hr	Flexibility [c] Length of Breaks, inches		Abrasion Resistance Taber Abrader Cycles
Kind of Film	Clear	Pigmented	Clear	Clear	Clear	Clear	Pigmented	Clear
IB(3)CS(1)	11	18	>60	>3	<3	None	1.8	100
CP(1.4)CS(1)	39	29	> 5<10 (>60)[d]	>216	>2.5	0.6	1.6	175
CP(1.5)CL(1)	50	36	> 5<10 (>20<30)[d]	>216	>144	0.5	1.5	225
DCP(3)CL(1)	76	50	< 5	>216	>144	1.5	3.0	300 (800)[e]
CP(2.6)IB(1)CL(1)	58	38	> 5<10	192	......	0.4	2.4	350[e]

[a] Plate Glass 100.

[b] Caustic used was 5% NaOH in water. A watch-glass was placed on the panel, convex side up, and the caustic solution introduced under the watch-glass, on the coating surface. Fresh caustic solution was added as needed to replace that lost by evaporation, which was practically negligible. The criterion for failure was any blistering, dissolution of film, loss of adhesion, or other obvious deterioration. Softening of the film was also noted by scratching lightly with the fingernail.

[c] The conical mandrel used for the flexibility test is that described in ASTM method D522-60, and furnished by Gardner Laboratories. Angle of cone is estimated as 10°. Breaks measured to the closest one-eighth.

[d] No drier.

[e] Pigmented.

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[1] Presented at the AOCS meeting in St. Louis, Mo., 1961.

[2] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

TABLE III

Changes in Sward Hardness of Films-Plate Glass 100

Polymer Film	Air-Drying		Baking at 450F–15 min
	2 weeks	3 weeks	
CP(1.4)CS(1)	34	34	39
CP(1.5)CL(1)	28	34	50
DCP(3)CL(1)	28	44	76
CP(2.6)IB(1)CL(1)	20	26	58

Low Temperature Baking

DCP(3)CL(1)	180F–20 min	225F–30 min
Immediate	16	32
After 2 days	48	50

Procedures and Discussion

End-Use Application

Investigations were made on five selected polymers (Table I) to determine their suitability for architectural, wrinkle and small-appliance finishes, coating for cans and wire, and adhesives. As a part of these investigations, weight loss and chemical changes during baking, chemical resistance of baked films, changes in color ratings and reflectance and compatibility with other resins were studied.

Architectural, Wrinkle and Small-Appliance Finishes. Four of the five polymers dried to hard clear films at room temperature overnight, and hardness continued to increase for several weeks. In Table III DCP(3)CL(1) illustrates results obtained with all four, except that its films were somewhat harder and continued curing for a longer period. The high content of the dicyclopentadienyl group probably accounts for this phenomenon, and the DCP(3)CL(1) polymers baked to hard, clear films at comparatively low temperatures and short periods of time.

Air-drying and baking properties displayed by the samples suggested their possible use in architectural and small-appliance finishes; consequently, tolerance for several commonly used pigments, fillers and colors was determined. The polymers were compatible with TiO_2 (R-610), $CaCO_3$, talc, clay, silica (caused one to gel), toluidine maroon, carbon black and chrome green. The polymers caused flocculation of titanium-calcium, mica and phthalocyanine blue.

Wrinkle finishes suitable for some small-appliances were comparatively easy to obtain with these polymers in gray, red and green tints. Driers (0.01% Co and 0.5% Pb) were necessary to obtain wrinkling, and addition of 0.01–0.03% Zn drier did not eliminate it. The wrinkle finishes were produced on air-drying and were very tough and appealing to the eye.

Studies on exterior exposures are continuing. Results so far indicate that pigmentation and baking improve durability. Both air-dried and baked clear films completely deteriorated on exterior exposure in approximately one year. Pigmented films, especially the darker colors, had much better durability; the majority of panels still showing no visible damage after exterior exposure at 45°, facing south for two years. The exposure of these panels is being continued.

TABLE IV

Dielectric Strengths of Vinyl Ether Films

Polymer film	Volts/mil
IB(3)CS(1)	660
CP(1.4)CS(1)	410
CP(1.5)CL(1)	610
DCP(3)CL(1)	800
CP(2.6)IB(1)CL(1)	650
Commercial phenolic resin	470

TABLE V

Cut-Through or Temperatures Required for Shorting Coated Wires under Stress

Polymer film	Temperature for start of resistance decrease-F	Direct short-F
IB(3)CS(1)	400	450
CP(1.4)CS(1)	425	450
CP(1.5)CL(1)	440	>525
DCP(3)CL(1)	>550	>550
CP(2.6)IB(1)CL(1)	>550	>550
Commercial phenolic resin	420	480

Wire Coatings. Dielectric strengths were determined according to ASTM D-149-59 (short term) using steel panels coated by drawdown with approximately 1 mil dry film thickness and baked at 450F for 15 min. The dielectric strengths of these films (11) and of a proprietary phenolic coating are given in Table IV. Because of these promising dielectric strengths, tests were conducted with annealed copper wire. The wire was drawn through a polymer solution and a heated chamber to effect the desired amount of coating and degree of baking. Coatings had poor flexibility and poor adhesion to copper by this method; however, the films appeared to have good continuity as determined electrically. Wire coated with these polymers could not be readily soldered unless the coating was removed mechanically. Cut-through values (11) were superior to the commercial phenolic resin. Table V summarizes data regarding the cut-through tests.

Can Coatings. Previous studies have shown that films of certain polymers of fatty vinyl ethers have unusual flexibility and adhesion (9). If these properties could be retained and superior resistance to foods achieved, the polymers would merit further exploration as coatings for tin, aluminum, or black iron cans. Tests with CP(1.4)CS(1) and DCP(3)-CL(1) showed that after baking at 400F for 30 min, or 450F for 15 min, stamping operations caused considerable damage in areas of severe deformation. Microscopic examination and checking for porosity of the films with copper sulfate solution revealed damage that was not apparent on casual visual examination. Additional work is in progress aimed at polymer compositions having improved flexibility and adhesion. Styrenated polymers showed some promise in can stamping and forming operations (7,11).

Adhesives. The only polymer to show fair metal-to-metal adhesion was DCP(3)CL(1). However, the bond strength was found to be considerably lower than that obtained with an epoxy-polyamide control. This poor metal-to-metal bond strength for vinyl ether polymers is probably caused by the almost complete exclusion of oxygen from films during curing. In tests in which the joint was separated, the polymer was still soft and tacky, indicating that very little, if any, curing had occurred. Some potential was apparent for either metal-to-wood or metal-to-paper adhesion for specific polymers, but

TABLE VI

Weight Changes in Vinyl Ether Films on Baking at 400F for 60 min

Polymer film	Molar ratio of modifier to fatty vinyl ether	Wt loss %
CP(3)IB(1)CL(1)	4/1	0.0– 0.5
CP(1.5)CL(1)	1.5/1	3.6– 4.0
CP(1.4)CS(1)	1.4/1	9.9–10.6
CP(2)IB(1)CL(1)	3/1	5.4– 7.0
DCP(3)CL(1)	3/1	7.2
CP(0.7)CL(1)	0.7/1	13.8–15.7
CL	0	20.8
CS	0	32.0

they did not show any significant advantage over presently available proprietary systems.

Certain Properties of Polymers and Films

Weight Loss and Chemical Changes. Weight loss of either homopolymers or copolymers of soybean and linseed vinyl ethers during baking was high, with weight loss from soybean being the higher. Introduction of increasing amounts of cyclic monomer, with or without other saturated vinyl ethers, substantially lowered weight losses. Weight changes of certain selected polymers on baking 60 min at 400F are shown in Table VI. Weight loss was roughly proportional to the amount of fatty vinyl ether present.

An infrared study of chemical changes occurring in baking the polymer film was undertaken to determine the reasons for these weight losses. Variations in drier composition and inclusion of antioxidant were tried. The following statements summarize infrared data (Table VII):

1) Carbonyl content on the carbon attached to the ether group (C=O at 8.55 μ) increased and the ether content (C—O—C at 9.2 μ) decreased with increasing amounts of baking or air oxidation. Apparently methylene groups adjacent to the ether oxygen were oxidized to ester groups. Chemical studies on lauryl isopropyl ether support this observation (6).

2) Chemical changes continue after an initial baking at 400F for 60 min.

3) Hydroxyl and/or peroxide content appear to remain constant.

4) Manganese drier promotes the most ester formation of the driers tried; lead drier promoted the least ester formation—even less than no drier at all.

5) Drier plus antioxidant promotes less ester formation and less ether decrease than drier without antioxidant.

Oxidation of polymer films appears to continue for extended periods but can be reduced in amount by use of lead drier and antioxidant. Attack occurs at the methylene group adjacent to the ether linkage, and probably at unsaturated bonds, but data supporting attack at the latter in the baking films are lacking.

Chemical Resistance. Chemical resistance of baked films to a number of household products was fair to good with polymers containing cyclic structures. Tests include resistance to oils and detergents, and results are summarized in Table VIII.

Color Ratings and Reflectance on Initial Exposure to Ultraviolet. Very marked lightening and increases in reflectance occurred when clear or pigmented films were exposed to ultraviolet light. The degree of lightening was measured with a Gardner Color-difference meter (11). Three values were determined with this instrument: Rd, a, and b. Rd or luminous reflectance value is the degree of reflectance in percent; value a indicates redness when plus, gray when zero, and greenness when minus; value b shows yellowness when plus, gray when zero, and blueness when minus.

Reflectance of pigmented films was generally higher than that of clear films, but the change after 14 days was less. Redness changes rapidly after exposure, approaching zero in both clear and pigmented films. Yellowness decreases in all pigmented films becoming 15 or less after 14 days. Cyclopentadiene polymers increased in yellowness in clear films but followed the trend in pigmented films. Color changes were generally acceptable for architectural finishes. Values of Rd, a and b obtained by Color Difference measurements for three selected polymers are reported in Table IX, covering areas which were unexposed, exposed to ultraviolet light for 14 days, and covered by aluminum foil for 14 days.

TABLE VII

Chemical Changes in Vinyl Ether Polymer IB(3)CS(1) as Indicated by Infrared Absorption [a]

Drier	Baking Time at 400F min	Increase in Optical Density at Wave Lengths Characteristic of			
		OH hydroxyl 2.88 μ	C=O ester 8.55 μ	C—O—C ether 9.20 μ	Ratios of densities $\frac{\text{C—O—C}}{\text{C=O}}$
None	15	0.041	0.170	0.321	1.88
	60	0.042	0.197	0.301	1.53
Mn, 0.05%	15	0.039	0.223	0.316	1.42
	60	0.043	0.24	0.293	1.19
	60 [b]	0.056	0.248	0.293	1.19
	60 [b,c]	0.056	0.278	0.284	1.02
Pb, 0.50%	15	0.032	0.159	0.352	2.22
	60	0.037	0.185	0.302	1.63
	60 [b]	0.049	0.210	0.318	1.51
	60 [b,c]	0.062	0.239	0.306	1.28
Mn, 0.05%+	15	0.040	0.206	0.327	1.59
antioxidant [d]	60	0.043	0.232	0.306	1.32

[a] Absorption bands were corrected to a constant (0.500) optical density of the CH_2 (3.42 μ) absorption band.

[b] Followed by 2 weeks' air-dry.

[c] Followed by an additional 60 min bake at 400F.

[d] "Pip-Pip"—Monosanto Chemical Co., St. Louis, Mo.

Compatibility with Other Resins. Compatibility of vinyl ether polymers with other resins was investigated by blending a 50% solution in toluene of the ether polymer in question with 50% solutions of each of 20 commercial resins dissolved in solvents

TABLE VIII

Chemical Resistance of Baked Films (450F for 15 min) of Selected Polymers

Chemical Product		Films of									
		IB(3)CS(1)		CP(1.4)CS(1)		CP(1.5)CL(1)		DCP(3)CL(1)		CP(2.6) IB(1)CL(1)	
Mineral	Cl [a]	F	1 [b]	F	24 [b]	F	16 [b]	←	No effect after 500 [b]	→	
spirits	Pg [a]	F	3	←			No effect	500	→		→
Ethyl	Cl	F	11	F	1	F	16	No effect	500	F	8
alcohol	Pg	F	11	F	1	←	No effect	500	→	F	300
Lemon	Cl	Sl. dark	500	←		No effect	500	→		Sl. darker	500
juice	Pg	F		No effect		Sl. dark	500	No effect	500	Sl. darker	500
NaOH–5%	Cl	F	300	F	100	←	No effect	500	→	Darker	500
	Pg	Dark	24	Dark	500	←	Sl. dark	500	→	Darker	500
Detergent–1%	[c] Cl	F	200	←		No effect			→	Sl. darker	500
Mineral oil	Cl	Sl. spotty	24	Sl. spotty	500	←	No effect	500	→	Sl. darker	500
	Pg	Sl. dark	500	Sl. spotty	500	←	No effect	500	→	Sl. darker	500
Coffee	Cl	F	200	No effect	500	←		Sl. dark	500		→
	Pg	Darker [d]	24	Sl. dark	500	←		Sl. dark	500		→
Water	Cl	←			No effect	500		→		Sl. darker	500

[a] Cl—clear; Pg—pigmented; Sl—slightly; F—failed in.

[b] Numbers refer to hours of exposure.

[c] TIDE, Procter and Gamble Co., Cincinnati, Ohio; no effect means that immersion gave no perceptible change in blushing, whitening, swelling or other physical alteration.

[d] Stained.

TABLE IX

Reflectance and Color Changes in Clear and Pigmented Films as Determined by the Color Difference Meter

Polymer	Pigmentation	Unexposed			Covered 14 Days[a]			Exposed to UV[b] 14 Days		
		Rd	a	b	Rd	a	b	Rd	a	b
		Re[c]	Red	Yellow	Ref	Red	Yellow	Ref	Red	Yellow
DCP(3)CL(1)	Clear	50	6	36	55	2	33	65	—2	25
	Pigmented	70	0.5	19	71	—1	17	79	—3	8
CP(1.4)CS(1)	Clear	15	22	28	20	20	28	60	0	33
	Pigmented	40	7	22	45	6	20	70	0	15
CP(1.5)CL(1)	Clear	19	21	30	25	17	30	60	1	31
	Pigmented	43	7	22	45	6	20	70	0	14

[a] This section of the panel covered with aluminum foil during the exposure to UV.

[b] General Electric type S-1 sun lamp was placed 12 in from panel surface. Panels were placed on a rotating table and a fresh lamp was used after every 72 hr of operation.

[c] Ref = Reflectance.

known to be compatible with vinyl ethers. Blends were made at ratios of 1:9 and 9:1 by volume. A number of these blends resulted in clear, haze-free solutions. However, hydrogenated rosin was the only resin to produce clear, wrinkle- and tack-free films. This lack of compatibility is somewhat surprising. The compatibility with recently prepared styrenated vinyl ether polymers varies but is improved, and appears to be associated with composition of the vinyl ether polymer, as well as with the extent of styrenation. Research is now being conducted on the styrenation reaction and on properties of the polymers from it (7,11).

ACKNOWLEDGMENT

This is a report of the work done by Battelle Memorial Institute under contract supervision of the Northern Regional Research Laboratory with the U.S.D.A., authorized by the Research and Marketing Act. Samples of soybean and linseed fatty alcohols supplied by Archer-Daniels-Midland Co.

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[Received February 16, 1962—Accepted June 6, 1963]

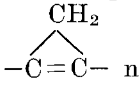
Methods for the Determination of Cyclopropenoid Fatty Acids. I. Aqueous Hydrochloric Acid Method[1]

F. C. MAGNE, J. A. HARRIS, and E. L. SKAU, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

Abstract

An analytical method is described for the estimation of long-chain cyclopropenoid fatty acid derivatives. It is based upon the quantitative addition of a molecule of hydrogen chloride at the cyclopropene ring when the sample is shaken with concentrated hydrochloric acid. The cyclopropenoid content can be calculated, as sterculic acid, from the increase in chlorine content. Epoxy compounds and hydroperoxides interfere and must be removed by one of the accepted pretreatment methods.

Introduction

THIS IS ONE of a series of reports resulting from a search for improved methods for the quantitative determination of long-chain cyclopropenoid fatty acids. These acids, which respond to the Halphen test, contain the group  $-\overset{CH_2}{C=C}-$ near the middle of the carbon chain. In sterculic acid, a 19-carbon acid which is the major fatty acid constituent of *Sterculia foetida* seed oil, this group is in the 9-10 position. The cyclopropenoid acid which is present as a minor constituent in cottonseed oil fatty acids has been reported to be predominantly malvalic acid, the corresponding 18-carbon acid with the cyclopropene group in the 8–9 position (1,2,3).

A number of methods of analysis have been suggested. Deutschman and Klaus (4), and Shenstone and Vickery (3), used modifications of the Halphen color test. Gas chromatographic analysis was applied by Miwa et al. (5) to the methyl esters, and by Smith, Wilson, and coworkers (6,7) to the methyl esters after dihydrogenation of the cyclopropene ring.

Another method, developed by Smith, Wilson, et al. (6,7,8), involves titration with a standard solution of hydrogen bromide in glacial acetic acid (Durbetaki reagent) after first destroying the epoxy acids by lithium aluminum hydride reduction or cold acetolysis. The number of moles of hydrogen bromide added equals the number of moles of cyclopropenoid moiety present. The titration is time-consuming and unsatis-

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[1] A laboratory of the So. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.