

TABLE III
Oils and Fats Consumed as Food (1952)

	Weight (mil.lb.)	Percent- age	Lbs. per capita
Spreads			
Butter (fat content).....	1,080	15.9	7.0
Margarine (fat content).....	975	14.3	6.3
	2,055	30.2	13.3
Cooking fats			
Lard.....	1,816	26.6	11.7
Shortenings.....	1,562	23.0	10.1
	3,378	49.6	21.8
Salad oils, etc.	1,373	20.2	8.8
Total.....	6,806	100.0	43.9

food and the total fat intake. If we can accept as typical a 2,500-calory diet which runs 20-25% fats, such as has generally been recommended, it indicates the consumption of about 92.5 lb. of fat per year. This would mean that the 43-44 lb. of visible fats we use in the U.S.A. is somewhat less than half the total of our food fats. Presumably the Indians and the Chinese who average a very low consumption of visible fats, as indicated earlier, get an even larger proportion of their total as non-visible fats, but we have no information on that point.

The fats used for non-food purposes have averaged about 24.7 lb. during recent years, but last year the total was 21.6 lb. The breakdown of this latter figure is shown in Table IV.

TABLE IV
Non-Food Fats Consumed (1952)

Uses	Weight (mil. lb.)	Percent- age	Lbs. per capita
Soap.....	1,203	36.0	7.7
Drying oils.....	914	27.0	5.9
Other industrial uses.....	1,236	37.0	8.0
Total.....	3,353	100.0	21.6

Summarizing the above information, we conclude that the world as a whole suffers from a chronic deficiency in fats and the supply is so short that most of the visible fats are used as food, leaving only minor amounts for non-food uses such as soap, paint, etc. Any marked increase in the living standards of the more populous areas of the world will probably change the latter from exporting to importing areas and will sharply reduce the supply available to Europe and the other importing nations. The supply of visible fats can be materially increased but not enough to satisfy the needs of the people, and it is doubtful that it can increase fast enough to gain on the rapidly increasing world population.

In contrast with the world's limited fat supply and unfavorable prospects for the future the U.S.A. now has, and should continue to have, an adequate supply. We have an adequate supply because there is a demand for vegetable oils for certain food products even at premium prices. At the same time the animal fats, representing the larger share of our total production and coming as necessary by-products from the meat we eat, continue to be produced in large volume. As a result we are able to consume on a per capita basis three times the world average consumption and still have a surplus. Parenthetically it might be pointed out that this surplus has tended to accumulate in the United States rather than to move into export channels in normal fashion due to financial and other controls applied by foreign governments.

REFERENCES

1. Information taken from bulletins of the Office of Foreign Agricultural Service, The Fats and Oils Situation published by the Bureau of Agricultural Economics, and miscellaneous published sources.

[Received May 19, 1953]

Esters of Polyallyl Alcohols as Protective Coating Vehicles¹

R. P. COX,² R. D. JERABEK, and J. C. KONEN, Archer-Daniels-Midland Company, Minneapolis, Minnesota

THE allyl grouping has been studied extensively by oil chemists for the purpose of producing industrially useful allylic esters of fatty acids. A few of the approaches involve consideration of the following potentialities:

- a) Esterification of monomeric drying oil fatty acids with allyl alcohol followed by polymerization of the monomeric esters.
- b) Esterification of polymeric fatty acids with allyl alcohol.
- c) Esterification of monomeric drying oil fatty acids with polymeric allyl alcohol.

This laboratory (16) in 1944 prepared the allyl ester of linseed fatty acids by alcoholysis of linseed oil. This ester was purified by double distillation. Attempts to polymerize the crude or purified products to give a drying oil were largely negative, using organic peroxides such as benzoyl peroxide and tertiary butyl hydroperoxide at high catalytic levels. Teeter and Cowan (15) reported the preparation of the allyl esters of polymeric soybean fatty acids by direct es-

terification and the corresponding ester from dilinoleic acids by alcoholysis of methyl dilinoleate. These products likewise possessed only a limited capacity for copolymerization.

Allyl alcohol is quite stable at temperatures below 100°F. undergoing neither polymerization nor other changes for long periods (14). Bradley (5) describes a procedure for preparing polyallyl alcohol by the passage of oxygen through purified allyl alcohol, maintained near the refluxing temperature. Products prepared by this process varied from 5 to 16 hydroxyl groups per molecule, depending upon the experimental conditions. Other methods of polymerizing allyl alcohol have been reported, including saponification of diallyloxalate (11), the peroxide-induced polymerization of allyl acetate (3), the use of a polymerization accelerator, *e.g.*, diallyl ether, under the influence of heat and pure oxygen (6), and the emulsion polymerization of allyl acetate (15).

Polyallyl alcohol is generally considered to contain one double bond per molecule and the structure is believed to be linear with each hydroxyl group primary. This polyhydric alcohol is soluble in water, alcohols, glycols, and only slightly soluble in hydrocarbons. It

¹Presented at the Fall Meeting, American Oil Chemists' Society, San Francisco, Calif., Sept. 26-28, 1950.

²Present address: Cargill Inc., Minneapolis, Minn.

readily forms poly esters and alkyd resins and undergoes other known reactions of polyhydroxy compounds (14). For example, Bradley (5) prepared improved drying oils from linseed, soybean, or cottonseed fatty acids by direct esterification of the fatty acids with a polyallyl alcohol having at least five esterifiable primary hydroxyl groups per molecule. Similar claims were made for an oil obtained by the interaction of polyallyl alcohol and dehydrated castor oil fatty acids (6).

The present paper represents a summation of the research study initiated in 1947 on the problem of investigating the oil up-grading potentialities of polyallyl alcohol.³

Experimental

Preparation of Vehicles. The reaction of the polyallyl alcohols with the fatty acids or oil was carried out, using three general procedures:

a) Direct esterification was performed under vacuum at a maximum temperature of 450°F. until the acid value was 5.0 or less for non-viscous oils or 12.0 or less for samples which exceeded 5 stokes in viscosity during processing.

b) Alcoholysis at atmospheric pressure with varying levels of polyallyl alcohol was carried out under nitrogen at a temperature of 450-475°F. for 1-3 hours using 0.10% of calcium naphthenate, based on the oil, as the catalyst. Fatty acids equivalent to 90% of the excess alcohol were then introduced, and esterification was completed under vacuum as above to give mixed glycerol-polyallyl esters.

c) Alcoholysis under vacuum following the above procedure resulted in the removal of 54-70% of the total glycerol, following which the excess hydroxyl groups were esterified with fatty acids by the standard vacuum esterification procedure.

Evaluation of Vehicles. The various liquid products were controlled and evaluated by standard analytical procedures for acid value (10), Gardner color (8), viscosity (1), Sanderson film set-up time (in vehicle, unless otherwise indicated, the driers were 0.20% of Pb and 0.025% of Co added as the naphthenates) (12), and vehicle or paint consistencies (9). Similarly, certain techniques were employed which have become standard for use in the evaluation of dried clear or pigmented films, including such properties as Sward hardness (13), Kauri flexibility (7), water or alkali resistance (1), Weatherometer durability (16), gloss and gloss retention (2), and compatibility with modifying agents.

Results and Discussion

Analytical characterization of the various grades of polyallyl alcohol is given in Table I and illustrates several points of structural variation in the different polymers. As the number of polymer units increases from X-201 through X-301, the consistency varies from a heavy syrup to a frangible solid. With an increase in molecular weight there is an increase in I. V. and a loss of hydroxyl groups per unit of weight for the first three polyols. X-501 has a lower I. V. than the other types and has a higher hydroxyl content. The preferred type of polyallyl alcohol from the suppliers viewpoint was X-101, and therefore it received the most attention in this work.

³The samples of polyallyl alcohol were supplied by the Shell Development Company, Emeryville, Calif.

TABLE I
Analytical Data on Various Samples of Polyallyl Alcohols

	Type of Alcohol			
	X-201	X-101	X-301	X-501
Av. mol. weight.....	462	550	650	900-950
Units per molecule.....	8.0	9.5	11.0	16.5
Av. hydroxyls per molecule.....	6.0	6.5	5.5	13.0
A. V.	1.1	1.1	1.3	1.2
I. V. (WIJS).....	35.0	50.0	72.5	9.0
Softening point (°C.).....	59.0	72.5

Linseed and soybean esters prepared by direct vacuum esterification are included in Table II. The properties of the esters vary markedly with the complexity of the alcohol. The linseed esters 1 and 2 from X-101 and X-201 had much lower acid values and viscosities than the ester 3 prepared from the more functional polyallyl alcohol, X-501. Correspondingly the gel times and set-up times of the linseed esters of X-101 and X-201 were much slower than the X-501 ester. The effect of the base acids is displayed by a comparison of products 1 and 4, and the linseed ester gelling at 600°F. in approximately half the time and drying in two-thirds the time of the corresponding soybean ester although the viscosities and acidities were quite comparable.

TABLE II
Polyallyl Alcohol Esters of Linseed and Soybean Fatty Acids

	Product number				
	1	2	3	4	5
Reactants					
Linseed acids.....	75.3	76.5	78.3
Soybean acids.....	75.3	78.3
Polyallyl alcohol					
Type.....	X-101	X-201	X-501	X-101	X-501
%.....	24.7	23.5	21.7	24.7	21.7
% excess.....	8.8	11.9	9.0	8.8	9.0
Properties of esters					
Acid value.....	1.5	4.3	11.1	2.4	11.7
Color (Gardner).....	9-10	9-10	11-12	10	8-9
Visc. (Stokes).....	4.2	5.2	40.8	4.7	19.5
Gel time (min.).....	33	31	1	62
Set-up time ^a (hrs.).....	2	1¾	¾	3	1¼

^a Driers. 0.2% of Pb and 0.025% of Co added as naphthenates.

The linseed and soybean esters of polyallyl alcohol X-101 were evaluated as varnish vehicles in 30-gallon pentaerythritol ester gum and 10-gallon maleic resin varnishes. In the pentaerythritol ester gum series (Table III) the linseed X-101 and the soybean X-101 esters were compared with commercially available maleic anhydride treated linseed oil and soybean oil controls. The linseed ester as compared with the modified linseed oil control was slower cooking, comparable in color and water resistance, and definitely superior in speed of dry, hardness of dry, flexibility, and alkali resistance. A comparison of the soybean X-101 ester and the linseed control illustrates the interesting fact that the synthetic soybean ester was equivalent or superior in every case except cooking speed and varnish color.

Maleic resin varnishes are compared in Table IV as baking vehicles against the corresponding dehydrated castor oil-maleic resin control. White enamels from the linseed and soybean poly ester varnishes were slightly superior to the control in hardness and color stability of aging. The three enamels were rated equal and very good with respect to gloss.

The relatively high equivalent weight of the polyallyl alcohols which necessitated use of over 20% by

TABLE III

Evaluation of 30-Gallon P. E. Ester Gum Varnishes of Polyallyl Alcohol X-101 Linseed and Soybean Esters

	Base Oil			
	Linseed 24.7% X-101	Soybean 24.7% X-101	Commer- cial maleic linseed	Commer- cial maleic soybean
Min. at 580°F.....	72	104	49	66
Varnish characteristics at 50% N.V.				
Viscosity (Stokes).....	2.0	1.4	1.4	1.65
Color.....	13	17	12.5	13.0
Drying prop. ^a set-up (hrs.).....	2.3	3.0	4.3	4.0
Sward hardness				
24 hrs.....	24	22	22	14
1 wk.....	38	32	32	24
2 wks.....	42	32	34	26
Kauri				
Pass.....	60	60	50	50
Fail.....	70	70	60	60
Chemical resistance				
Rel. water resistance.....	V. G.	V. G.	V. G.	V. G.
3% NaOH (min.).....	4	4
Blush.....
Wrinkle.....	30	5
Fail.....	300	180	30	30

^a 0.4 Pb, 0.05% Co.

weight of the alcohol in esterifications with drying oil fatty acids prompted an examination of the mixed glycerol-polyallyl alcohol esters of soybean fatty acids. This type of mixed ester was most readily prepared by alcoholysis of the base oil with polyallyl alcohol X-101, followed by vacuum esterification of the excess of hydroxyl groups with fatty acids.

Experimental work on the preparation of the mixed esters of soybean fatty acids is summarized in Table V. Soybean oil was alcoholized with polyallyl alcohol, and the excess of hydroxyl groups was esterified to give products corresponding to the starting composition outlined in Table V for products 6 and 7. During the alcoholysis steps of 8 and 9 a major portion of the glycerol was removed by performing the reaction under vacuum.

The alcoholysis of soybean oil, using from 4 to 15% of X-101, was successful, but the more resinous and complex polyallyl alcohols, X-301 and X-501, would not undergo this reaction. Products 6 and 7 were distinctly superior to soybean oil in drying properties, and products 8 and 9, in which 14 to 15% of polyallyl alcohol was incorporated by removal of glycerin, were markedly superior.

It was thought that use of polyallyl alcohol, X-501, which did not react with soybean oil under alcoholysis conditions would be more effective than the lower polymers in upgrading and hardening soybean oil. Blends of soybean oil and an ester of soybean fatty acid containing 21.7% of X-501 were prepared as

outlined in Table VI. The evaluation of these blends as drying oils indicated that the incorporation of only 10.8% of polyallyl alcohol, X-501, into soybean oil by this technique results in an excellent upgrading of the base oil.

In a further attempt to utilize the desirable modifying qualities of polyallyl alcohols on soybean oil, a series of finished vehicles was prepared, consisting of the mixed esters of soybean fatty acids and rosin. These mixed esters were further modified in some cases with chemicals such as maleic anhydride, phthalic anhydride, or diallyl maleate. The syntheses were carried out by standard techniques consisting of vacuum esterification at 450°F. for 2-3 hours and 500°F. for 7-8 hours, following which the esters were bodied at 550-580°F. in 4-5 hours to a viscosity of approximately 20 stokes at 50% N.V. in mineral spirits. Substitution of polymerized rosin for resin or X-301 for X-101 made no fundamental difference in the processing conditions.

TABLE IV
Evaluation of 10-Gallon Maleic Resin Varnishes of Polyallyl Alcohol Esters

	Base Oil		
	Linseed X-101	Soya X-101	D.C.O.
Min. at 580°F.....	51	75	72
Physical properties at 50% N.V.			
Viscosity.....	4.35	1.65	2.5
Color.....	13	15	12
Baking of enamels for 30 min.			
at 260°F. ^a	18	16	14
Sward hardness.....	EX.	EX.	EX.
Gloss.....
Color rating			
Fresh.....	2	2	1
Aged.....	1	1	2

^a TiO₂, PVC of 19%, 0.05% Co metal as naphthenate.

A screening evaluation of mixed soybean fatty acid-rosin esters covering a wide range in composition is indicated in Table VII, using a commercially available soybean oil copolymer as a control. Sample 16, containing 46.6% of soybean fatty acids, 31.2% of wood rosin, and 22.2% of X-101, represents the maximum quantity of fatty acids which can be utilized to give air-dry hardness approaching the control. The substitution of a polymerized rosin in vehicle 17 for wood rosin in vehicle 16 resulted in only a slight improvement in air drying. Vehicle 19 with a fatty acid control of 42.4% represents a sub-minimum level since the film was extremely hard and brittle.

TABLE V
Mixed Polyallyl-Glycerol Esters Prepared by Alcoholysis of Soybean Oil Followed by Esterification of Excess Hydroxyl Groups With Soybean Fatty Acids

	Product Number						
	6	7	8	9	10	11	12
Proportion of components							
Soybean acids.....	93.0	89.3	83.2	81.9	83.5 ^a	87.0 ^a	93.9 ^a
Glycerol.....	8.7	8.45	3.4 ^b	2.3 ^c
Polyallyl alcohol.....	3.9	7.2	13.8	14.9	16.5	13.0	6.2
Type.....	X-101	X-101	X-101	X-101	X-301	X-501	X-501
Properties of ester							
Acid value.....	5.5	6.4	3.2 ^d ^d ^d
Color (G).....	6.7	6.7	10-11
Viscosity (Stokes).....	1.0	1.0	1.7
Set-up time (hrs.).....	5½	4¾	3	4

^a As oil.^b 54% of glycerol in starting oil removed during alcoholysis.^c 70% of glycerol present in starting oil removed during alcoholysis.^d Alcoholysis with oil failed.

TABLE VI

Properties of Blends of Soybean Oil With the Polyallyl Alcohol X-501 Ester of Soybean Fatty Acids

Composition of blend	90	80	70	50	0
Soybean oil.....	10	20	30	50	100
Soybean X-501 esters.....	2.1	4.3	6.5	10.8	21.7
X-501 in blend %.....					
Properties of blends					
A. V.....	1.4	2.5	3.6	5.8	11.7
Color (G).....	6-7	6-7	7	7-8	8-9
Visc. (Stokes).....	0.7	1.0	1.3	1.4	19.5
Set-up (hrs.).....	6	4¾	3¾	2	1¼
Film qualities.....	Poor	Poor	Good	Excellent	Excellent

Baking tests on the same group of vehicles are shown in Table VIII. Substitution of polymerized rosin in vehicle 17 for wood rosin in vehicle 16 gave a marked improvement in baked film hardness in addition to the slight improvement previously noted for air drying. Substitution of polyallyl alcohol X-301 in vehicle 18 for X-101 in vehicle 15 resulted in superior baking performance. Again, vehicle 19 with a fatty acid content of 42.4% represents a subminimum level, giving bad wrinkling during baking. All of the vehicles with a fatty acid content below 55% were compatible with urea-formaldehyde resins.

The results as shown above indicate that the optimum level of soybean fatty acids is approximately 47%. The preferred type of resin, especially from the viewpoint of baking properties, is polymerized

rosin, and polyallyl alcohol X-301, if available, would be the most efficient type of alcohol.

Additional work is described in Table IX with particular emphasis on utilization of polymerized rosin and polyallyl alcohol X-101. At levels of 61% and 54%, respectively, of soya fatty acids in vehicles 20 and 21 the films were soft and alkali resistance was poor. At 47% of soya fatty acids with polymerized rosin in vehicle 22 and wood rosin in vehicle 23 the products were comparable in hardness of dry and chemical resistance. Use of tall oil in vehicles 28 and 29, especially the former, gave satisfactory film hardness, but water and alkali resistance were quite inferior. The control was superior in all respects except color and flexibility.

In an attempt further to improve the baking characteristics of the mixed soybean fatty acid-rosin esters, low levels of maleic anhydride, phthalic anhydride, or diallyl maleate were considered. The products (Table X) modified by these chemicals are quite comparable to the unmodified control (vehicle 21).

The use of urea-formaldehyde resin as a hardening agent was considered in the last five entries of Table X. Without added resin the copolymer vehicle showed greatest hardness, with the alkyd control and the more highly rosin modified ester vehicles being equivalent. Again the polymerized rosin vehicle (22) shows su-

TABLE VII

Air-Dry Characteristics of Several Mixed Soybean Fatty Acid-Rosin Polyallyl Esters

	Product Number							
	13	14	15	16	17	18	19 ^a
Vehicle composition								
Soya Acids (%).....	68.5	61.7	55.0	46.6	47.1	56.0	42.4	
Rosin								
Type ^b	Wood	Wood	Wood	Wood	Polym.	Wood	Wood	
%.....	7.5	15.4	23.5	31.2	31.4	14.0	28.3	
Polyallyl alcohol								
Type.....	X-101	X-101	X-101	X-101	X-101	X-301	X-301	
%.....	24.0	22.9	21.5	22.2	21.5	30.0	29.3	
Properties at 50% N.V.								
A. V.....	7.2	6.7	11.7	10.0	7.4	9.7	11.4	1.1
Color.....	9-10	12-13	9-10	9-10	10-11	11-12	10-11	14
Viscosity.....	3.0	2.25	1.4	1.4	1.5	2.0	1.4	2.1
Air-dry film sward hardness ^c								
24 hr.....	2	6	12	22	24	14	34	40
1 wk.....	4	10	20	36	40	20	50	56
Kauri flexibility								
Pass.....	110	80	60	10	10	70	10
Fail.....	120	90	70	20	20	80	0	20

^a Commercial soybean oil dicyclopentadiene copolymer.

^b W. G. wood rosin and poly-pale resin (products of the Hercules Powder Co., Wilmington, Del.).

^c 0.0015 inch drawdowns on glass, 0.2% Pb. and 0.025% Co.

TABLE VIII

Baking Characteristics of Several Mixed Soybean Fatty Acid-Rosin Polyallyl Esters

	Product Number							
	13	14	15	16	17	18	19 ^a
Vehicle composition								
Soya acids (%).....	68.5	61.7	55.0	46.6	47.1	56.0	42.4	
Rosin								
Type.....	Wood	Wood	Wood	Wood	Polym.	Wood	Wood	
%.....	7.5	15.4	23.5	31.2	31.4	14.0	28.3	
Polyallyl alcohol								
Type.....	X-101	X-101	X-101	X-101	X-101	X-301	X-301	
%.....	24.0	22.9	21.5	22.2	21.5	30.0	29.3	
Baking properties ^b								
30 min. at 250°F.								
Rel. tack.....	Heavy	Heavy	Heavy	Light	Light	V. Light	T. F.	T. F.
Wrinkle.....	Sl.	V. Sl.	V. Sl.	No	Sl.	Sl.	Heavy	No
15 min. at 300°F.								
Sward hardness.....	2	4	6	12	20	12	22	14
Urea formaldehyde resin compatibility ^c								
Solution.....	No	No	OK	OK	OK	OK	OK	No
Film.....	No	No	OK	Fair	OK	OK	OK	No

^a Commercial soybean oil dicyclopentadiene copolymer.

^b 0.0015 inch drawdowns on glass, 0.02% Mn.

^c Ratings based on observations of clarity of systems containing 30% Uformite.

TABLE IX
Varnish Evaluation of Mixed Soybean Fatty Acid-Resin Esters of Polyallyl Alcohol X-101

	Product Number						
	20	21	22	23	28	29 ^a
Vehicle Composition							
Soya Acids (%).....	61.5	54.2	47.1	46.6	
Resin							
Type.....	Polym.	Polym.	Polym.	Wood	Tall oil ^b	Tall oil ^c	
%.....	15.4	23.3	31.4	31.2	74.8	74.6	
Polyallyl Alcohol							
Type.....	X-101	X-101	X-101	X-101	X-101	X-101	
%.....	23.1	22.5	21.5	22.2	20.4	20.6	
Other							
Type.....	Diallyl Maleate	Diallyl Maleate	
%.....	4.8	4.8	
Characteristics of 50% N.V. Vehicles							
Color (Gardner).....	8-9	9-10	10	10	12	11-12	14
Viscosity (Stokes)							
Fresh.....	2.5	1.3	1.3	1.65	1.25	1.5	2.1
1 month.....	2.4	1.4	1.4	1.65	2.5
Set-up (hrs.).....	6.5	6.8	6.8	5.5	5.6	5.5	3.3
Sward hardness							
24 hr.....	4	10	20	24	20	8	24
2 wk.....	14	28	40	44	42	28	48
Kauri							
Pass.....	100	70	30	10	20	40	10
Fail.....	110	80	40	20	30	50	20
Chemical resistance							
Water.....	Fair	Good	Good	Good	Poor+	Poor+	Ex.
3% NaOH (min.).....							
Blush.....	5	5	10	10	1	1	48 hrs.
Wrinkle.....	10	10	20	20	3	3
Fail.....	30	30	120	120	5	7	100+hrs.

^a Commercial soybean oil dicyclopentadiene copolymer.

^b Refined tall oil containing 22% of rosin acids.

^c Refined tall oil containing 35% of rosin acids.

periority over wood rosin, vehicle 23, in hardness. The urea-formaldehyde resin modification upgraded the hardness of the wood rosin-based vehicle and the alkyd control, but degraded the polymerized rosin vehicle and the copolymer control.

In colored baking enamels vehicle 22 had good baking characteristics. It gave a balance of properties, comparing favorably with the controls, being intermediate in hardness, alkali resistance, gloss and gloss retention, and superior in consistency stability on aging. Vehicle 20 resulted in soft films for baking pur-

poses, but the lengthening of the fatty acid content to 61.5% confers excellent durability characteristics, being equal to the alkyd in gloss retention and check resistance.

Conclusions

1. The polyallyl alcohols were found to be typical polyhydroxy compounds in esterification reactions with soybean, linseed, and rosin acids.
2. Alcoholysis of soybean oil to give mixed glycerol-polyallyl esters proceeded only with simpler poly-

TABLE X
Baking Properties of Clears and Enamels From Various Soybean Fatty Acid-Rosin Esters of Polyallyl Alcohol X-101

	Product Number									
	21	24	25	26	27	20	22	23 ^a ^b
Vehicle composition										
Soya acids (%).....	54.2	51.2	50.7	43.8	51.6	61.5	47.1	46.6		
Resin										
Type.....	Polym.	Polym.	Polym.	Polym.	Polym.	Polym.	Polym.	Wood		
%.....	23.3	22.0	21.7	29.2	22.2	15.4	31.4	31.2		
Polyallyl alcohol										
Type.....	X-101	X-101	X-101	X-101	X-101	X-101	X-101	X-101		
%.....	22.5	24.7	24.3	23.6	21.4	23.1	21.5	22.2		
Other										
Type.....	None	Maleic	Phthalic	Phthalic	Diallyl Maleate	None	None	None		
%.....	2.1	3.3	3.4	4.8		
Baked properties clear^c										
Sward hardness.....	36	40	38	48	28	14	46	30	56	40
Urea-formaldehyde resin addition %.....						30	10	10	10	20
Sward hardness.....						22	34	40	24	46
Compat.....						Fair	Fair	Good	Poor	Good
Baked enamels^d										
Sward hardness.....						10	28	20	34	26
Alkali resistance (min.).....						5	40	32	90+	8
60° Gloss ^e										
Initial.....						88	86	90	91	82
609 hrs.....						65	46	39	16	65
Checking rating ^f						10	3	3	3	10
Consistency stability (K.U.)										
Fresh.....						73	62	61	66	94
2 months.....						85	62	63	74	104

^a Commercial soybean dicyclopentadiene copolymer.

^b Commercial medium phthalic castor alkyd.

^c 0.0015 inch drawdowns, 30 min, at 300°F., 0.03% Mn.

^d Aquamarine enamel at 12% PVC; 67/16.5/16.5-TiO₂/iron blue/med. chrome green.

^e Values obtained after 0.0 and 609 hours' exposure in a National Carbon X-1A Weatherometer.

^f Observations at 100X magnifications after 609 hours' exposure in Weatherometer with ratings on a scale of 0 for complete failure to 10 for no checking.

ols whose size did not exceed an average of 9.5 allyl alcohol units.

3. Polyallyl alcohol proved to be an excellent oil upgrader, the mixed glyceryl polyallyl esters of soybean oil at a 10-15% polyallyl alcohol level were superior to linseed oil in film properties. Complete soybean or linseed esters containing 21-25% of polyallyl alcohol were found to be superior to standard soybean and linseed varnish oils in 30-gal. pentaerythritol ester gum varnishes and equivalent to dehydrated castor in short length maleic resin varnishes.

4. A soybean fatty acid-rosin polyester prepared from 47.1% of fatty acids, 31.4% polymerized rosin and 21.5% of polyallyl alcohol X-101 was equivalent to a soybean oil copolymer or a medium oil length castor alkyd as a baking enamel vehicle.

Acknowledgment

The authors gratefully acknowledge the assistance of R. M. Brice of this laboratory in the preparation of the vehicles.

REFERENCES

1. A.S.T.M. Standards, 1947 Supplement, Part II, Designation: D-154-47.
2. A.S.T.M. Standards, 1949, Part IV, Designation: D-523-49T.
3. Bartlett, P. D., and Altschul, R. J., *J. Am. Chem. Soc.*, **67**, 1812-16 (1945).
4. Bartlett, P. D., and Nazaki, K., *J. Polymer Science*, **3**, 216-22 (1948).
5. Bradley, T. F. (to American Cyanamid Co.), U. S. Patent 2,378,827 (1945).
6. British Patent 573,757 (to American Cyanamid Co.) (1945).
7. Federal Specifications TT-P-141b, January 15, 1949, Method No. 415.1.
8. *Ibid.*, Method No. 424.8.
9. *Ibid.*, Method No. 428.1.
10. *Ibid.*, Method No. 507.1.
11. Muskat, I. E., and Pollack, M. A. (to Pittsburgh Plate Glass Co.) U. S. Patent 2,332,460 (1943).
12. *Proc. A.S.T.M.* **26**, Part II, 556 (1926).
13. Scientific Section Circular No. 510, 223 (1936).
14. Shell Development Company, "Allyl Alcohol," *Tech. Publ. SC*, **46**, 32 (1946).
15. Teeter, H. M., and Cowan, J. C., *Oil and Soap*, **22**, 177-80 (1944).
16. Unpublished data.

[Received April 22, 1953]

The Pigmentation of "Red" Cottonseed Oils

CATHERINE HALL POMINSKI, PATRICIA VON DER HAAR, and ROBERT T. O'CONNOR, Southern Regional Research Laboratory,¹ New Orleans, Louisiana, and W. T. COLEMAN, West Texas Cottonoil Company, Abilene, Texas

THE price obtainable by the cottonseed processor for his oil is a direct function of the red color of that oil when refined, since he is required to market his oil on the basis of the red color of the refined product (4). Consequently the processor is necessarily concerned with the problem of controlling the development of red color in the crude oil or reducing it to a minimum by refining. In most cases little difficulty is encountered in reducing the red color of a crude oil to an acceptable level by standard refining and bleaching techniques. Occasionally, however, the removal of the red color of certain oils does present a serious problem. For example, oils produced from seed grown in certain areas of West Texas and oils processed under slightly abnormal conditions which tend to develop high red color on storage ("reverting" oils) are very difficult to refine and bleach to a low red color. Despite the interest of the cottonseed industry in "red" color there is little information available concerning the pigments in the oil which are responsible for such color development.

This investigation was initiated in an effort to obtain some information concerning the pigments responsible for red color in cottonseed oils and to attempt to render a typical highly-colored crude cottonseed oil more amenable to standard refining and bleaching techniques by converting the pigments responsible for red color to forms readily removable with alkali.

The unusually high red color of the screw-pressed cottonseed oil produced in a mill in West Texas during the 1950-51 processing season provided an opportunity for such an investigation. To obtain an oil for comparison, the corresponding seed from which this screw-pressed oil had been processed was expressed in a

pilot-plant hydraulic press without the application of heat. The screw-pressed oil and its corresponding seed were shipped by air mail immediately after the oil was collected from the presses so that the samples were less than 24 hours old when this investigation was begun. Both the screw-pressed oil and the cold-

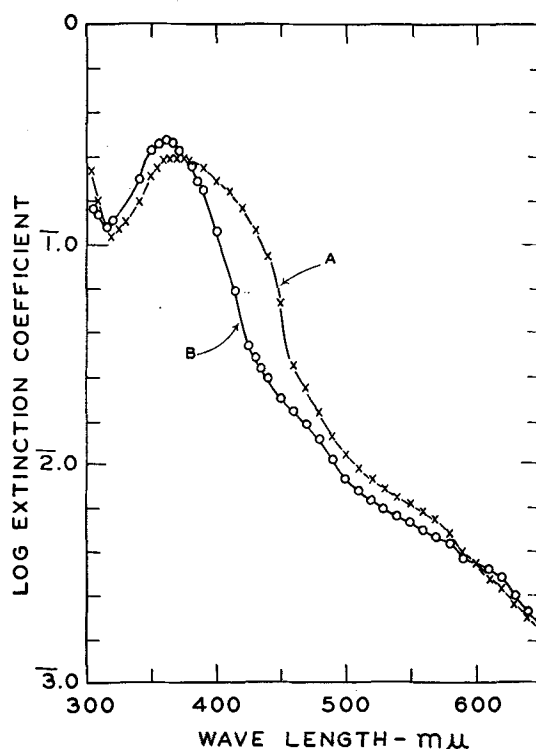


FIG. 1. Absorption spectra of the crude screw-pressed cottonseed oil in iso-octane solution (A) untreated and (b) after treatment with 0.5 N HCl.

¹ One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture, New Orleans, Louisiana.