ing toward the lower range of the curve where the change in density per unit concentration of gossypol is greater than for higher concentrations; hence the calculated free gossypol content is too low. To avoid this error it is necessary to calculate the apparent free gossypol content of both solutions (A and B) and then subtract the value obtained for solution A from that for solution B to obtain the free gossypol content of the sample aliquot.

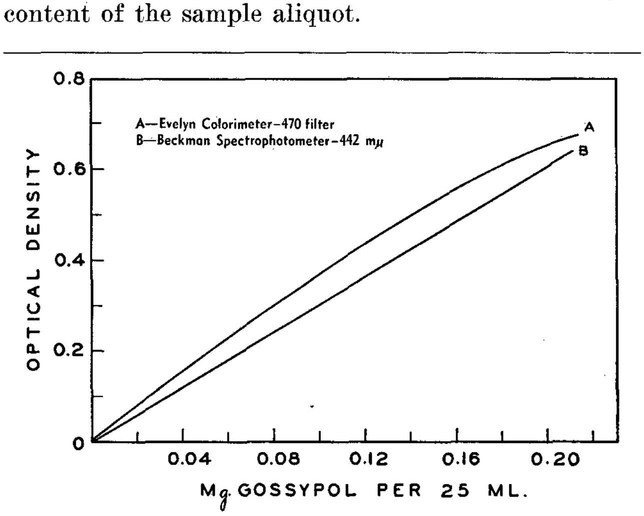

FIG. 6. Calibration curve for the reaction of gossypol with aniline.
A—Evelyn colorimeter—470 filter
B—Beckman spectrophotometer—442 mμ

Summary

A method is proposed for the determination of free gossypol in chemically treated cottonseed meals containing dianilinogossypol. The procedure includes a rapid qualitative test for detecting the presence of dianilinogossypol in cottonseed meals.

Investigation of the properties of dianilinogossypol showed that it was appreciably soluble in water-free solvents, such as acetone, methyl ethyl ketone, or chloroform, but only slightly soluble in 70% acetone, an efficient solvent for the extraction of free gossypol.

Both 70% acetone extracts of chemically treated meals and pure dianilinogossypol in the same solvent exhibited significant changes in optical density due to slow hydrolysis of dianilinogossypol. Dilution of aqueous acetone extracts with 80% isopropyl alcohol produced changes in optical density even greater than those occurring in undiluted extracts, introducing serious errors in the free gossypol determination.

The addition of a small amount of aniline to the aqueous acetone for extraction stabilized the extract against changes in optical density and yielded constant values for free gossypol over a period of several hours. Use of aqueous acetone without aniline gave values which increased with the time interval between extraction and analysis. Extrapolation of these values to zero time gave results in good agreement with those obtained by the use of aqueous acetone containing aniline.

The intense background color in extracts of chemically treated meals introduces a source of error when photoelectric colorimeters yielding non-linear calibration curves are used for analysis. A modification in the customary method of calculation eliminates this source of error.

Acknowledgments

The authors are indebted to Robert T. O'Connor and Donald Mitcham for the spectrophotometric data and to Lawrence E. Brown for the nitrogen determinations. Appreciation is also expressed to W. J. Miller of the Buckeye Cotton Oil Company for the samples of chemically treated meals.

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Evaluation of "Hysoy" in Exterior Paints[1]

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IN A SERIES of publications (1, 3-7), Teeter, Cowan, and coworkers have described a method of preparing drying oils by chlorination of soybean oil with *t*-butyl hypochlorite, and subsequent dechlorination either by heating in a vacuum or by reaction with aqueous solutions of weakly basic salts. The products contained dienoic, trienoic, and tetraenoic conjugation, and, as would be expected, they dried very rapidly (set-to-touch time, 20-30 min.) with formation of wrinkled or frosted films. Although such oils tended to be dark in color, dried films were colorless. This bleaching effect was observed even when films were allowed to dry in total darkness. For convenience, these oils were named "Hysoy" oils.

In order to evaluate more thoroughly the utilization of Hysoy in protective coatings, a memorandum of understanding was negotiated in March 1949 between the Northern Utilization Research Branch and Paint Research Associates Inc. Although the evaluative studies were originally planned to include both exterior paints and varnishes, the investigation of varnishes was dropped when it was found that residual chlorine in the oil was slowly liberated (as hydrogen chloride) at varnish-cooking temperatures,

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[1] Presented at the Fall Meeting of the American Oil Chemists' Society, Oct. 11-13, 1954, in Minneapolis, Minn. The mention of firm names or trade products in this article does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

[2] Correspondence should be addressed to this author because Mr. Lewis has retired from the U.S.D.A.

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resulting in serious discoloration of the varnishes. Unfortunately no method of dechlorination could be found that would reduce the amount of residual chlorine below about 1%.

This paper therefore is limited to a presentation of the results obtained during evaluation of Hysoy in exterior paints.

Preparation of Oil Sample

Soybean oil (35.5 lbs.) was chlorinated with *t*-butyl hypochlorite to a level of 8.45% chlorine in pilot-plant equipment. It was then dechlorinated thermally in the apparatus described by Bell and Teeter (1). The product had the following constants: Cl, 3.89%; acid value, 6.23; viscosity (Gardner), S-T; color (Gardner), off scale; conjugation: diene, 12.6%; triene, 10.0%; tetraene, 1.6%; total, 24.2%.

Formulation of Exterior Paints

Six exterior white paints were prepared. Pigments and driers used are given in Table I. Composition of the vehicles and viscosity data for the finished paints are shown in Table II. Pigment volume concentration for these paints is 33.5%. Drying times for the paints, as determined on the Sanderson drying machine (2), also are indicated in Table II. All samples were discarded after three years and two months of storage. During this period slight increases in viscosity (2 to 3 K.U.) occurred. Each paint showed some medium hard settling but could easily be stirred back into a uniform consistency. No corrosion of the cans was observed.

TABLE I

Non-Oil Components of Exterior Paints

	Lbs.	Gal.
Anatase titanium dioxide (Titanox A LO)	138	4.23
Magnesium silicate (Nytal 300)	322	13.58
35% leaded zinc oxide (Lehigh 61)	461	9.50
Min. spirits	117	18.00
Lecithin	2.5	0.25
24% Pb Naphthenate	6.3	0.66
6% Co Naphthenate	0.9	0.11
6% Mn Naphthenate	0.45	0.05

Preparation of Panels for Exposure

Six 6-in. bevel siding panels of red cedar wood were painted in three coats. Three days elapsed between the prime coat and the second coat, five days between the second and third coats, and approximately eight days between the third coat and the date of exposure. Five of the panels were painted in such a way that a 6-in.-wide area of PRA–1 could be compared with an 18-in.-wide area of each of the other paints. The remaining panel was painted to permit comparison of a 6-in.-wide area of PRA–4 with an 18-in.-wide area of PRA–1. The two areas on each panel were separated by a black dividing line.

Results of Exposure Tests

The six panels, prepared as described, were exposed at Peoria, Ill., to outdoor weathering tests at a 90° angle, facing south, from August 16, 1949, to September 3, 1953, except for a short time in the spring of 1950 when the panels were returned to Chicago, Ill., for inspection by Paint Research Associates Inc.

Details of the condition of the panels after three and a half months and after four years of exposure may be summarized as follows:

CONDITION AFTER THREE AND A HALF MONTHS

Panel No. 1; PRA–1 vs. PRA–3. Both films were in good condition. PRA–3 had a slightly heavier dirt retention.

Panel No. 2; PRA–1 vs. PRA–6. Both films were in good condition. PRA–6 had slightly heavier dirt retention.

Panel No. 3; PRA–1 vs. PRA–4. Both films were in good condition. PRA–4 had more dirt retention.

Panel No. 4; PRA–1 vs. PRA–5. Both coatings had similar dirt retention. PRA–5 showed embryonic cracking in the brush markings.

Panel No. 5; PRA–1 vs. PRA–2. PRA–2 showed cracking and wrinkling in the craters of the brush marks where there is an excess of paint. There was noticeable dirt retention by both coatings.

Panel No. 6; PRA–4 vs. PRA–1. Results were the same as with Panel No. 3.

CONDITION AFTER FOUR YEARS

The following general observations can be made:

1. No outstanding differences were found among the six coatings studied.
2. All coatings chalked considerably and equally on rubbing gently with the finger.
3. No coating showed flaking or checking.
4. All coatings showed more or less horizontal cracking. These cracks are short, 0.5 in. or less, and the edges curl upwards to expose the wood but show no flaking. Most of the cracks occurred near the holes bored for the screws that held the panels on the fence, as well as near the vertical, black lines separating the two areas on each panel.
5. All coatings showed exposed or bare wood in certain areas, apparently due to chalking of the paint

TABLE II

Oils Used in Exterior Paints. Drying Times and Viscosities of Finished Paints

	PRA–1		PRA–2		PRA–3		PRA–4		PRA–5		PRA–6	
	Lbs.	Gal.	Lbs.	Gal.	Lbs.	Gal.	Lbs.	Gal.	Lbs.	Gal.	Lbs.	Gal.
Bodied LO (44")	173	21.60										
Raw LO	250	32.40										
Hysoy			434.7	54.00			217.4	27.00	326	40.50	108.7	13.50
Non-break SBO					250	32.40	125	16.20	62.5	8.10	187.1	24.30
Non-break bodied SBO (51")					173	21.60	86.4	10.80	43.2	5.40	129.6	16.20
Vehicle												
Linseed (%)	100											
Hysoy (%)			100				50		75		25	
Soybean (%)					100		50		25		75	
Viscosity, initial, K.U	99		114		98		....		....		....	
Viscosity, after 4 mo., K.U	100		105		100		102		105		101	
Drying time, hrs.[a]	4.67		1.67		9		1		1.5		5	

[a] Point at which sand brushed off.

from the bottoms of deep brush marks. This was again found principally near both sides of the black dividing line.

6. On the basis of general appearance the six coatings can be placed in the following order of decreasing merit: PRA–1, PRA–3, PRA–2, PRA–4, PRA–5, PRA–6.

Acknowledgment

The authors wish to express their gratitude to E. W. Bell of the Northern Utilization Research Branch for preparation of the Hysoy used in this investigation.

Conclusions

Hysoy and blends of Hysoy and soybean oil can be used successfully in the formulation of white exterior paints. Such paints compare favorably in outdoor weathering tests with similar paints made with linseed and soybean oils. The principal advantage shown by paints formulated with Hysoy is a decrease in drying time.

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ABSTRACTS . . . . R. A. Reiners, Editor

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor
Sin'itiro Kawamura, Abstractor

The influence of metallic impurities on the stability of palm oil. V. P. Rams. *Oleagineux* 10, 177-178(1955). The relatively low stability of palm oil as determined by the Swift or Schaal tests is very probably due in part to the presence of appreciable quantities of iron which originate from the attack of the free fatty acids on the containers. The addition of citric or phosphoric acid increases the stability of the oil presumably by forming inactive complexes with the iron compounds. The action of these deactivators is particularly noticeable for the fluid portion of the oil which contains less iron than the solid fraction. The addition of ascorbic acid produced no stabilizing effect.

The application of thermal methods of analysis to the detection of adulterated cocoa butter. S. V. Vaeck. *International Chocolate Review* 10, 1-7(1955). The standard method of Pichard and a new method of crystallization delay permit certain detection of an addition of 20% of any of the substitutes which have been investigated except for Borneo tallow. To determine the crystallization delay approximately 1 gram of fat is melted to a temperature of 50° to 60°C. and is then filtered through a small filter at the same temperature. A clean "U" shaped capillary tube is half filled with liquid fat by immersing one end and sucking on the other end. The tube is then sealed off at both ends. For a determination of the curve of crystallization delay, the whole tube is first placed in a bath of hot water (80°C. or more). The hot tube is transferred as expeditiously as possible to a controlled temperature water bath, the temperature of which is known to the nearest 0.1°C. This temperature is selected so as to be in the neighborhood of the melting point of the least stable polymorphic form of the fat (16° to 18°C. in the case of cocoa butter). The time that elapses before distinct clouding of the sample occurs is recorded (this requires powerful side lighting and a black background). The time is reckoned from the moment of plunging the tube into the water bath. The clouding must commence at the same instant along the whole length of the tube and not just at specific places. Should clouding not occur simultaneously at all points along the length of the tube, the tube has not been sufficiently cleaned or the fat contains traces of solid impurities; in either case, the result must be discarded. By repeating this test at different cooling temperatures (usually between 10° and 20°C.), one obtains a curve showing the crystallization delay as a function of cooling temperatures. This curve is also characteristic for the particular fat. It is sufficient in practice to determine the curve for delays of up to 20 seconds, as the reproducibility of values obtained at higher temperatures than are represented by this delay is not very satisfactory. Although the method of Pichard appears to be more sensitive in certain cases than that of crystallization delay, the latter test offers the advantages of a smaller sample requirement and more rapid determination of adulteration.

Extraction of carotene from palm oil. I. R. H. O. procedure. M. Servant and Miss Argoud. *Oleagineux* 10, 15-20(1955). The palm oil is preferably separated first into a liquid fraction and a fraction that is solid at ordinary temperatures by crystallization at 19° with the former fraction being enriched in carotene by this treatment. One hundred kilograms of the whole neutral oil or the liquid fraction described above is dissolved in methanol and transesterified. The washed esters are distilled in a molecular still, preferably of the centrifuge type, at a temperature of 80°-100° and a vacuum of 0.001 mm. The esters distill while about 2 kilograms of a concentrate containing about 115 grams of the carotenoids, 2% of the oil that did not undergo methanolysis and other unsaponifiables remain as the residue. This residue is saponified with 4 kilograms of an alcoholic solution of potassium hydroxide at a maximum temperature of 60° in an inert atmosphere. The mixture is dried and extracted with petroleum ether or dichlorethane. The solvent is evaporated under vacuum to give a new concentrate of unsaponifiables containing 25-30% of carotene. This concentrate is dissolved in benzene and precipitated by the addition of methanol. Further purifications of the crystallized carotene may be effected by chromatography. A semi-industrial run using essentially the above conditions is described. Possibilities of recovering the glycerine resulting from the methanolysis are discussed briefly.

Isopropyl myristate and its uses for pharmaceutical and other purposes. 1. Sources for preparation and application. 2. Its preparation starting from ucuuba fat. J. R. da Silva Jardim. *Olearia* 8, 193-202, 243-249(1954). Ucuuba fat is shown to be a rich source of trimyristin. This triglyceride is obtained in a yield of 30% and a high degree of purtiy by refluxing 200 grams of the crude ucuuba fat with 3.5 liters of ethanol allowing the mixture to crystallize at room temperature, filtering off the trimyristin and recrystallizing it successively from ethanol and isopropyl ether. Myristic acid is obtained from the trimyristin by saponification, acidification with hydrochloric acid and benzene extraction of the resulting product from the acidified mixture. The myristic acid is converted to the isopropyl ester by refluxing it with an excess of isopropanol in the presence of sulfuric acid as a catalyst. The excess isopropanol and the mineral acid are separated by water washing and the resulting crude ester is purified by treatment with decolorizing carbon in ethanol or by vacuum distillation. Formulations are given to illustrate the uses of isopropyl myristate in pharmaceutical and cosmetic preparations.

Molecular distillation and its applications in the fat industry. C. Paquot. *Olii Minerali–Grassi e Saponi–Colori e Vernici* 31, 205-211(1954). The theory and equipment used in molecular