fore, neutral fats and phospholipids were separated and the fatty acid composition of each determined.

The method of separation provided only a gross phospholipid fraction. This fraction contains all the muscle lipids which are not washed from silicic acid by chloroform. The values reported will be diluted by the proportion of the nonphospholipid moieties in each sample.

The data in Table III indicate that the phosphatides are a rich source of polyunsaturated fatty acids in the muscle lipids. Arachidonic acid, calculated as C_{18} and C_{20} tetraenoic acids, is found consistently in a greater quantity in the phosphatides than in the neutral fats. The distribution pattern was then found to be reversed in veal lipids where the linoleic acid content of the neutral fats exceeded that of the phosphatides by a manyfold factor. This was completely unexpected and no explanation can be made until further data have been obtained.

If the marbling fat is similar in composition to the depot fats, then the intramuscular fats of fatter animals would be expected to be more nearly like the depot fats. For more complete knowledge of the muscle lipid composition a study of leaner animals would seem desirable.

The above data on fatty acid composition are only a preliminary study in an attempt to detect trends. A more thorough investigation is in progress.

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Metal Soaps of Wool Wax Acids as Stabilizers for Plasticized Polyvinyl Chloride[1]

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Copper, magnesium, lead, nickel, cobalt, manganese, iron, chromium, cadmium, and barium soaps of the wool wax acid fraction have been tested as stabilizers for plasticized polyvinyl chloride polymers. Barium, cadmium, and lead soaps performed well in the light stability evaluations. In the heat aging tests barium, magnesium, lead, and nickel soaps were superior while cadmium, and manganese soaps performed poorly. The copper, cobalt, iron, and chromium soaps were ineffective.

Two tests for stability were employed: an accelerated light aging test and an accelerated heat aging test. Combinations of barium and cadmium soaps were tested for synergistic effects and found to be more effective as stabilizers than the individual soaps. Soaps made from fractions of acids by partitioning the whole wool wax acid fraction were also tested. Neither the hydroxy nor the non-hydroxy acid fraction soaps had as good stabilizing properties for PVC as those of the whole acid fraction.

A VERY LARGE NUMBER of substances, including a variety of metal soaps, have been used to stabilize plasticized polyvinyl chloride films against breakdown by heat and light.

This laboratory has been interested for some time in wool wax and its fractionation products. The unusual combination of acids (normal, iso, ante-iso, and hydroxy) comprising the wool wax acid fraction suggested investigating the use of their metal soaps as stabilizers for polyvinyl chloride. The only prior work on the use of wool wax acid metal soaps in this regard is that revealed in a patent by de Nie (1). The disclosure is concerned primarily with salts made from a methyl alcohol soluble fraction of wool wax acids and metals from the silver group (Analytical Group I—silver, mercury, and lead). The soaps of these metals presumably react with any photochemically or thermochemically released halide atoms to form insoluble halides and inhibit further deterioration of the polymer.

The present paper describes investigations of the use of wool wax acid metal soaps as stabilizers for plasticized polyvinyl chloride films. Soaps of the whole acid fraction as well as soaps of partitioned acid fractions were studied. The following soaps of the whole acid fraction were tested: Copper, magnesium, lead, nickel, cobalt, manganese, iron, chromium, cadmium, and barium. In addition to the soaps mentioned above, barium and cadmium soaps of the hydroxy and nonhydroxy acid fractions obtained by partitioning the whole wool wax acids fraction (2) were also evaluated. The preparation and properties of these soaps are described in an accompanying paper (3). Included in this study are comparisons of stabilizing properties of the wool wax acid metal soaps with those of barium and cadmium stearates and laurates. Accelerated light and heat aging tests were used to determine stability of the films. The comparisons of the relative stabilizing ability of the different systems were made by visual inspection and by light transmission measurements on the test samples when mounted on a white paper background.

Preparation of Test Films. Test films were prepared from: polyvinyl chloride (Geon 101) (65%); plasticizer (34 to 32%), and stabilizer (1 to 3%). Either di-2-ethylhexyl phthalate (DOP) or tricresyl phosphate (TCP) was used as the plasticizer. The Geon 101, plasticizer, and stabilizer were first dry mixed in a beaker, then milled on a heated two roll rubber compounding mill at 160C for 8 min. The fused sheet was then molded in a form (3 in x 6 in x 0.07 in) maintained at 150C and 1000 psi for 20 min and then allowed to cool at room temperature.

Light and Heat Stability. An Atlas Weather-

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[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Ometer, employing two carbon arc lamps with the samples rotating around the light source, was used to determine the light stability of the samples. The temperature was about 65C throughout the test periods. A sample was removed for inspection every 24 hr.

Heat stability tests were conducted in a mechanical convection oven maintained at 160C. Samples were withdrawn at 15 min, at 30 min, and thereafter at 30-min intervals.

A sample was judged to have failed in either the light or heat stability tests at the first visual evidence of a darker coloration, however slight. The data shown in Tables II and III show the time at which such a color change occurred.

Light Transmission Measurements. A Photovolt Corporation Model 610 reflectance meter equipped with an amber tristimulus filter was employed to determine light transmission of the samples. The meter was calibrated to read a maximum (75 scale units) when the light was reflected from the white paper background on which the samples were mounted. All readings were taken with the light passing through the samples and reflected from the background. There was a definite correlation between discoloration and light transmission. As the discoloration increased the light transmission value decreased.

Results and Discussion

The copper, magnesium, lead, nickel, cobalt, manganese, iron, chromium, cadmium, and barium soaps of the whole acid fraction were tested at a level of 1% of stabilizer in films plasticized with either DOP or TCP. The cadmium, nickel, barium, and lead soaps were the only soaps of this group that performed well in both heat and light stability tests, although the lead soap stabilized samples had a tendency to become opaque during heat aging. Generally, the DOP plasticized films had greater stability than those plasticized with TCP. Since the same soaps showed the best stability in both plasticizing systems, the bulk of the investigation was limited to films plasticized with DOP.

The effect of stabilizer concentration was determined for the cadmium, nickel, barium, and lead soaps by increasing the amount of soap incorporated into the polymer plasticizer mix to 2 and 3%. The greater the cadmium and barium content, the greater the stability. Stability decreased with an increase in nickel content. Although films stabilized with 2% of the lead soap did not discolor as much as those stabilized with 1%, they tended to become milky and opaque indicating incompatibility. But 3% of lead soap was so incompatible it could not be milled into the polymer-plasticizer mix. From the preceding, it is apparent that the barium and cadmium soaps are good stabilizers and are superior to the other metal soaps evaluated in this study. Consequently, the remainder of the investigation was confined to a study of the barium and cadmium soaps and their mixtures in varying ratios.

TABLE I

Analytical Values of Wool Wax Acid Fractions Used in Soap Preparation

	Whole acid fraction[a]	Hydroxy acid fraction	Nonhydroxy acid fractions		
			Fr. I	Fr. II	Fr. III
Saponification No.	166.1	......	......	......	......
Acid No.	166.2	169.9[b]	154.8[b]	179.9[b]	190.2[b]
Per cent hydroxyl	2.6	5.7	0.6	0.5	1.0

[a] Several samples of acids were used in the preparation of the soaps. The analysis represents average values.

[b] Calculated from the saponification number of the methyl ester.

TABLE II

Stabilization of DOP Plasticized Vinyl Resin with 1% Barium or Cadmium Soap

Fatty acid in soap	UV Light Stability		Heat Stability	
	Hours to color change[a] in Atlas Weather-Ometer		Hours to color change[a] in 160C oven	
	Barium Soaps	Cadmium Soaps	Barium Soaps	Cadmium Soaps
Wool wax	96	120	2	2
Wool wax hydroxy	72	96	2½	2
Wool wax nonhydroxy, Frac. I	96	120	1½	1
Wool wax nonhydroxy, Fract. II	96	96	1½	1
Wool wax nonhydroxy, Fract. III	96	72	1½	1
Stearic	96	96	2	1½
Lauric	72	96	2	1½
Ustabilized film[b]	 24	....	.... ¼	....

[a] Times reported are for first appearance of color change.

[b] Sample actually discolored on processing.

In the next phase separate tests were made with the barium and cadmium soaps of stearic, lauric, wool wax acids, and fractionated wool wax acids. The wool wax acid fractions were obtained by solvent partition and consisted of an hydroxy acid fraction and three nonhydroxy acid fractions. Analytical data for the hydroxy, nonhydroxy, and whole acid fractions are summarized in Table I.

The stearates were prepared from triple-pressed stearic acid, acid no. 214.8. The laurates were prepared from a commercial lauric acid (Neo-Fat 12), acid no. 286.7.

The relative stabilizing properties of the barium and cadmium soaps are shown in Table II.

From the data given in Table II it is readily apparent that the barium and cadmium soaps of the nonhydroxy acid fractions are relatively poor heat stabilizers. It is characteristic of cadmium soap stabilized films undergoing thermal degradation to show a sudden change—going from a colorless transparent film to an opaque black film.

The assistance obtained by using the reflectometer in the stability test measurements is demonstrated in Figure 1. In this figure are four representative curves illustrating the change in light transmission of samples undergoing heat degradation. The abrupt change in the cadmium soap stabilized film is quite evident (Fig. 1).

The synergistic effects of combinations of barium and cadmium soaps of the wool wax acid fractions were also studied. Mixtures of thes soaps in varying ratios were evaluated and the results are shown in

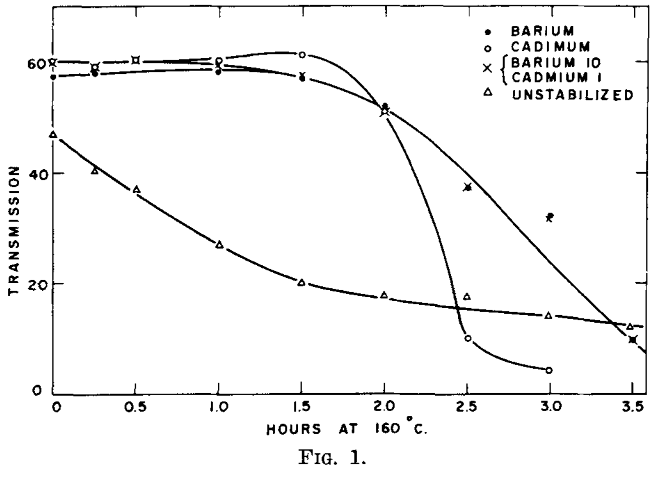

FIG. 1.

TABLE III

Stabilization of DOP Plasticized Vinyl Resin by Mixtures of Ba-Cd Soaps at a 1% Level

Ba-Cd Soaps	UV Light Stability Hours to color change[a] in Atlas Weather-Ometer			Heat Stability Hours to color change[a] in 160C oven		
Ratio	Wool wax	Lauric	Stearic	Wool wax	Lauric	Stearic
1/0	96	72	96	2	2	2
10/1	120	120	96	2	2	2
7/1	120	120	144	2	1½	1½
3/1	120	144	120	2	1½	1½
1/1	72	96	96	2	2	2
1/3	120	120	96	2	1½	1½
1/5	72	96	96	2	2	2
0/1	120	96	96	2	1½	1½

[a] Time reported is for first appearance of a color change.

Table III. Also reported in Table III are comparison tests with similar ratios of barium and cadmium soaps of lauric and stearic acids.

From the data given in Table III one can conclude that the mixed barium-cadmium soaps of lauric acid and those of the wool wax acids are effective as stabilizers in ratios from 3/1 to 10/1 (Ba/Cd). These mixtures are superior to the individual soaps in both heat and light stabilizing effectiveness. Synergism is demonstrated by two facts: discoloration of the film during heat aging is gradual compared to the abrupt change observed with cadmium soap stabilized films, and films stabilized with mixed soaps showed increased light stability compared to those stabilized with barium soaps.

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Sterculic Derivatives and Pink Egg Formation[1,2]

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Abstract

Sterculyl alcohol has been methylated and reduced to form the methoxyl and hydrocarbon derivatives. These two derivatives, sterculyl alcohol and the polymers of sterculic acid and methyl sterculate were fed to laying hens. The sterculic derivatives caused pink egg formation but the polymers did not.

The feeding of malvalic and sterculic acids to hens has been reported to cause pink discoloration in cold stored eggs (1,2). These acids give a positive Halphen test (3,4), which has been postulated to be specific for the cyclopropene ring (5). However, the property of derivatives of these fatty acids, such as the hydrocarbon or the alcohol, to produce these effects has not been reported.

Sterculic acid is sensitive to heat, forming a polymer the structure of which has been established (6). The loss of the characteristic infrared bands at 5.38 μ and 9.92 μ indicates that the cyclopropene ring is gone. Further evidence for this destruction is a negative Halphen test. The glyceride or methyl ester of the acid is considerably more stable to heat than the acid.

Nunn, in isolating sterculic acid (7), noted that the cyclopropene ring is resistant to lithium aluminum hydride reduction (LAH) by the method of Nystrum (8). This resistance was also observed by Smith (9) when LAH was used to differentiate cyclopropene fatty acids from oxirane oxygen-containing fatty acids. The cyclopropene ring has also been reported to be stable during saponification of *Sterculia foetida* oil at room temperature with 10% alcoholic KOH (1).

Very few methylation and reduction studies on fatty alcohols to form methyl ethers and hydrocarbons have been reported. Sekera and Marvel (10) reported preparation of saturated fatty acid tosylates in very good yields. Strating (11) prepared hexadecane from LAH reduction of cetyl tosylate in 98% yield. Although methoxy derivatives of hydroxy fatty acids and dimethoxy derivatives of fatty aldehydes have been reported in the literature, 1-methoxy-9-octadecene and similar compounds have not been hitherto reported. Studies of the methylation of sterculyl alcohol and oleyl alcohol with methyl iodide and silver oxide in dimethyl formamide revealed the presence of numerous side products. Methylation with methyl sulfate in tetrahydrofuran produced a methylated product in nearly quantitative yields.

The work reported in this paper shows that the hydrocarbon, ether, and alcohol of sterculic acid produce pink discoloration in eggs and give positive Halphen reactions.

Methods

Oil was extracted at room temperature from 2 kg of ground *Sterculia foetida* seeds[3] with Skellysolve F (3 x 3 l). The extracts were dried over anhydrous Na_2SO_4 and the solvent removed by distillation at room temperature under reduced pressure. The yield was 568 g of a golden yellow oil.

Transesterification. Transesterification of 200 g of *Sterculia foetida* oil was carried out at room temperature. The oil was added to 1 l of dry methanol containing 1% sodium methoxide. The heterogeneous solution was stirred rapidly for 45 min at which time the solution had turned homogeneous and a dark orange in color. The mixture was transferred to a separatory funnel and 500 ml diethyl ether was added followed by 250 ml of ice water. The aqueous layer was extracted with Skellysolve B (3 x 300 ml). The extracts were combined and washed with water (3 x 300 ml), 10% sodium carbonate (2 x 300 ml), 5% sodium bicarbonate (2 x 300 ml), and water (2 x 200 ml) to pH 7–8. The ether solution was dried over anhydrous sodium sulfate and the solvent removed on a rotovac. The yield was 186.5 g of methyl esters.

Fractionation. The methyl esters (125 g) were added to urea-saturated boiling methanol (125 g urea in 365 ml dry methanol). After 3 hr of occasional shaking the adducts were filtered and washed with 100 ml of urea-saturated methanol. Filtrate and washings were combined. A second urea adduct on the combined filtrate and washings removed essen-

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[1] Supported in part by National Cottonseed Products Association, Inc., Dallas, Texas.
[2] Arizona Agricultural Experiment Station Technical Paper No. 693.

[3] Seeds procured through the courtesy of F. R. Amos, Director of Forestry, Manila, Philippines.