tetrasodium pyrophosphate, the products were improved to the extent of approximately 25%.

Conclusions

In the foregoing discussion we have shown how tetrasodium pyrophosphate functions in soap mixtures. A summation of the advantages resulting from its use is given:

1. Tetrasodium pyrophosphate, when it constitutes 10 - 15% of the soap mixture, saves soap to the extent of 20 - 30% by completely preventing the magnesium ion from precipitating soap. At higher levels a partial elimination of the calcium ion will also result.
2. It reduces the insoluble soap content of the wash water by 20 - 30% because it reduces the magnesium and calcium ion content of the solution by this amount.
3. Because of these facts, more soap is made available for washing and dispersing the solids, less insolubles are present to complicate dirt removal, resulting in better washing solutions at no additional cost.

A Study of Factors Influencing the Color Contributed to Soap by Gum Rosin

By W. D. POHLE, Assistant Chemist, and C. F. Speh, Principal Chemist

NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING, UNITED STATES DEPARTMENT OF AGRICULTURE.

THE color of commercial soaps containing rosin varies from yellow to dark brown, depending upon the grade of fat and rosin used. Difficulty is sometimes encountered in reproducing a given color in the paler rosin soaps. To what extent and in what manner rosin contributes to this difficulty is not known. To the best of our knowledge, beyond the recognition of the existence of the problem, no particular stress is placed upon it in the literature of soap and soap making, although the problem has been encountered by the naval stores trade and manufacturers of soap. The fact that rosins of the same color grade do not always give the same results is not surprising as the color of the rosin is due principally to the length of face, kind and condition of cups, scrape and distilling practice, factors which are not related to the density, acid number, saponification number, or the other usual constants. These latter properties vary within a limited range for all grades of rosin and do not necessarily bear any relation to the color contributed to a soap by the rosin itself. In general, the lighter colored rosins will impart less color to soap than the darker ones.

Due to the absence of published methods for evaluating the color contributed to a soap by rosin, it was necessary to develop one for this purpose. The method adopted was applied to resin and rosin acids, modified resin and rosin acids, as well as to rosins and modified rosins.

A Method for Evaluating the Color Contributed to Soap by Rosin

The method developed involves two steps: (1) The preparation of a rosin soap by a method that resembles the full-boiled or settled soap process, rather than the semi-boiled or cold process, since the former is used most extensively in the manufacture of rosin soaps; and (2) Smoothing and measuring the reflectance of the rosin soap each week until the difference in weekly reflectance measurements is less than half the maximum variation between duplicate samples. The value is then recorded as the final reflectance of the sample.

Preparation of the Rosin Soap Cake

In a 400 ml. beaker, 70 ml. of water and rosin-free white stock soap (white floating soap, referred to later as stock soap) equivalent to 40 gm. of fatty acids were heated and stirred until homogeneous. The soap was then grained with 25 ml. of 34° NaOH and 10 gm. of freshly powdered rosin were added. To avoid oxidation the rosin should be powdered and weighed not more than 20 minutes before using. When the rosin was saponified and evenly distributed in the curd by boiling and stirring, the beaker was removed from source of heat and another 25 ml. of 34° NaOH added to complete the graining. Without being stirred the alkali was heated just to a boil, allowed to stand for a minute or two, and the settled lye removed with a pipette. Then with slight stirring the curd was washed by adding 35 ml. of water, warming the beaker at the same time. If this washing was carried out properly most of the wash water could be removed with a pipette. Then sufficient water was added (usually 30 to 35 ml.) to give the soap the proper smooth consistency when it is heated to boiling with stirring. The beaker was then placed in a water bath maintained at 82° to 84° C. for eight hours. At the end of this period the liquid soap was poured into a mold and allowed to solidify. The mold was a metal ring 2-1/2 inches in diameter and 5/8 inch high, set on a glass plate. The rosin soap prepared as described above filled the mold and the resulting soap cake when dry fits the photo-electric photometer. After the soap had solidified, that extending above the ring was sliced away with a sharp knife. If reflectance measurements on the wet soap cake are desired, this gives a smooth surface.

The method for preparing the rosin soap cakes might be varied in several ways without changing the method fundamentally. Any good grade of fat that will produce a white soap might be saponified, grained and used in place of the white stock soap. The rosin could be added to the soap stock before it is first grained with alkali, but this procedure did not yield as homogeneous soap curds and uniform rosin soap cakes as the method described. The following variation was also tried: The stock soap in 70 ml. of water was grained with 10 ml. of 34° NaOH, 10 gm. of freshly powdered rosin added, mixed thoroughly by boiling and stirring, and placed in a water bath (82° to 84° C.) for one hour. When removed, it was grained with 100 ml. of 25 per cent NaCl solution, and again placed in the water bath for one hour to permit complete graining. The salt solution was then removed, 50 ml. of water added, boiled, stirred and placed in the water bath for eight hours. Rosin soaps prepared by this modification appear to dry more slowly, have less color contrast among the lighter colored soaps, and are lighter in color than the rosin soaps prepared by the method adopted. Although graining with salt is more comparable with manufacturing practice, we chose NaOH for this purpose, as it accentuates the color rosin gives to soap, and thereby makes the detection of differences and measurements of the lighter colored rosin soaps easier and more accurate.

Evaluation of the Color Contributed to Soap by Rosin in Terms of a Reflectance Measurement

Photo-electric measurement of the reflectance of a soap cake for blue light of wave length 436 mu was found to provide a rapid and convenient method for evaluating the degree of coloration of the soap. A photo-electric photometer[1], designed by Dr. B. A. Brice (*1, 9*), using a mercury lamp with a filter to isolate blue light (wave length 436 mu), using 45° illumination and normal viewing of the sample, and giving apparent reflectance in terms of an MgO surface, was used.

Since a numerical figure for expressing darkness or darkening of the soap was desired, all measurements of reflectance were converted to the form — log B or log 1/B (B is the reflectance of the soap compared to an MgO surface using blue light 436 mu). This figure (—log B) was called the darkness index of the rosin soap, and in this form corresponds approximately to the darkening as judged visually. The darkness of a rosin soap may be considered as composed of two factors: (1) The color contributed by the soap stock and (2) the color contributed by the rosin. An index of the latter was obtained by subtracting the darkness index of a soap cake made with the soap stock alone from the darkness index of the rosin soap, containing 20 per cent rosin and 80 per cent fatty acid. This difference was called the soap darkening index of the rosin.

Table I gives the appearance of the rosin soaps, the darkness index of the rosin soaps, and the soap darkening index of the rosin. The darkness index of the soap stock was 0.4[2].

TABLE I
Relation between Appearance of Rosin Soap, Darkness Index of Rosin Soap and Soap Darkening Index of Rosin.

Color of Rosin Soap	white	white to light yellow	light yellow	yellow	dark yellow, orange, or dark yellow-brown or dark brown
Darkness Index of Rosin Soap (-log B)	less than 0.4	0.4 to 0.65	0.65 to 0.9	0.9 to 1.15	1.15 or more
Soap Darkening Index of Rosin	0.0	0.0 to 0.25	0.25 to 0.50	0.50 to 0.75	0.75 and higher

Blue light (wave length 436 mu) rather than green light (wave length 546 mu) or red light (approximate wave length 620 mu) was chosen for measuring the reflectance of the rosin soaps since it gave the best correlation between appearance and reflectance measurements and showed greater distinction between the medium and lighter colored rosin soaps. The calculated correlation coefficient (8) for reflectance measurements using blue light and visual arrangement of the samples was 0.989. This indicates an excellent correlation between the visual arrangement and instrument measurements.

For the darker samples, the green reflectance (G) of the rosin soaps was found more suitable than the blue reflectance (B), since the green reflectance was greater and showed greater distinction between samples. However, for the purpose of the present investigation, distinction between the darker samples is not so important and therefore since a blue reflectance measurement was found best for the medium and lighter colored rosin soaps it was used for all the reflectance measurements reported in this paper.

On the —log B scale duplicate rosin soap samples having darkness index values between 0.4 and 1.10 (soap darkening index of rosin between 0.0 and 0.70) showed an average difference of 0.02 and a maximum difference of 0.05. Greater differences appeared when the darkness index of the rosin soap and soap darkening index of the rosin were greater than 1.10 and 0.70.

A freshly prepared rosin soap cake kept in a desiccator over water at room temperature came to equilibrium in 48 hours, and under these conditions remained constant over a period of weeks and was not affected by different atmospheres (air, nitrogen, oxygen). When the rosin soap cake was removed and permitted to lose water, its reflectance became less and reached a practically constant value in 3 to 5 weeks, depending upon atmospheric conditions of temperature and humidity. The atmosphere (air, N_2 or O_2) in which the soap cake lost moisture, did not appear to influence its final color.

From the above it is evident that a reliable reflectance measurement can be obtained on a rosin soap cake 48 hours after molding, if it is kept in an atmosphere saturated with water vapor, whereas it requires 3 to 5 weeks when the soap cake is permitted to dry. However, under the former condition color differences between samples are only slight, and while some classification of the moist samples would be possible, the larger color differences existing between the dried samples permit a much more accurate evaluation of the reflectance of the rosin soap and the soap darkening index of the rosin.

The rosin soap cakes were soft when taken from the mold but began to lose water immediately. After drying one week or more in the laboratory a smooth level surface for the reflectance measurement was obtained by rubbing the cake gently with a circular motion on a fine wire screen (16 mesh). As the cake lost moisture it became darker, thus making it necessary to smooth the cake and measure its reflectance each week until the weekly change in reflectance was less than half the maximum variation between duplicate samples. The value was then recorded as the final reflectance of the sample. The final reading was usually obtained during the third to fifth week.

Color Contributed to Soap by Gum and Rosin Constituents

The non-volatile portion of the gum consists of resin acids and resenes (neutral compounds and compounds difficult to saponify). The resin acids (about 90 per cent of this fraction) are divided into two general groups — those that crystallize readily from the gum (the pimaric type acids); and those that do not crystallize readily from the gum (the sapinic

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[1] This instrument was loaned to us by R. W. Frey of the Hide Tanning Materials and Leather Section of the Industrial Farm Products Research Division.

[2] If two rosin soaps have the same darkness index, for example 1.15, and the darkness indexes of the fatty acid soap stock alone are 0.4 and 0.9 it is apparent that the color contributed by rosin in these two cases is not the same. The darkness index of rosins, when different soap stocks are used, cannot be compared.

types acids). Dextro- and laevo-pimaric acid (*2, 3* and *14*) and proabietic acid (*11*) have been obtained from the crystalline portion of the gum. Less is known about the sapinic acids, although it is believed that they make up the greater part of the resin acids of the gum (*4*). Recently Fleck and Palkin (*7*) have shown that dihydroabietic acid is present in the gum and the rosin of longleaf and slash pine.

Rosin made by processing the gum in the usual manner contains unchanged d-pimaric acid, some l-abietic acid, and unidentified intermediate acids produced by the action of heat on the resin acids (*13*). The l-abietic acid can be converted to pyroabietic acid by heat alone (*5, 12*), or catalytically (*6*). It is not likely that there is any appreciable quantity of pyroabietic acid in rosin, as the temperature favorable for its production is higher than that reached in the distillation of gum.

Various resin and rosin acids were evaluated for the color they contribute to soap by the method described above. These acids were also exposed in the form of a powder to air at room temperature for one week, and then evaluated. This period was found sufficient to produce appreciable oxidation of the more unstable resin and rosin acids. The acids studied were also heated in a sealed tube at a temperature of 180°C. for five hours and then tested. The temperature of 180° and five-hour period were chosen in order that the heat effect would be a little more pronounced than that to which the resin acids are subjected in the commercial production of rosin.

The treatment described above, applied to rosin made from longleaf gum collected in raised clay cups, gave the following results: The untreated rosin was grade N, and had a soap darkening index of 0.64. After heating as described above, its grade was M$^+$, and had a soap darkening index of 0.74. After exposing as described above, the grade was B and the soap darkening index was 1.17.

These tests show that further exposure of the rosin to heat does not appreciably affect the grade of rosin or soap darkening index, but that oxidation of certain acids present in the rosin has a marked effect on both.

Crystalline Gum Acids (Mixed Pimaric Acids)

The procedure followed in fractionating these acids was a modification of the method described by Palkin and Harris (14). The gum from the longleaf pine (collected in raised clay cups) was partly filtered by putting the gum in a suspended sack overnight. The crystalline portion in the bag was diluted with sufficient turpentine (10 parts gum — 1 part turpentine) to make it fluid enough to pour. This mixture was then centrifuged. The cloth used to retain the crystalline portion in the centrifuge permitted the passage of the liquid gum and the finer crystalline material. The crystalline material retained in the centrifuge was washed with 80 per cent alcohol, removed, dissolved in 95 per cent alcohol warmed to 50° C., filtered, and cooled to permit crystallization (Fraction C-1). The crystalline gum acids recrystallized from 95 per cent alcohol were converted to the sodium salt and purified by recrystallization from water. Flow Sheet I outlines the fractionation of both the crystalline and non-crystalline gum acids. The gum acids were obtained from the sodium salt by adding a slight excess of 2N acetic acid to a cold alcoholic solution of the sodium salt which was then diluted with cold distilled water. The gum acids were separated by filtration and dried in a vacuum oven at 40° C.

Rosin soaps were prepared from Fractions C-1, C-2, C-3 and C-4 before and after treatment as described above. The results are summarized in Table II.

TABLE II.

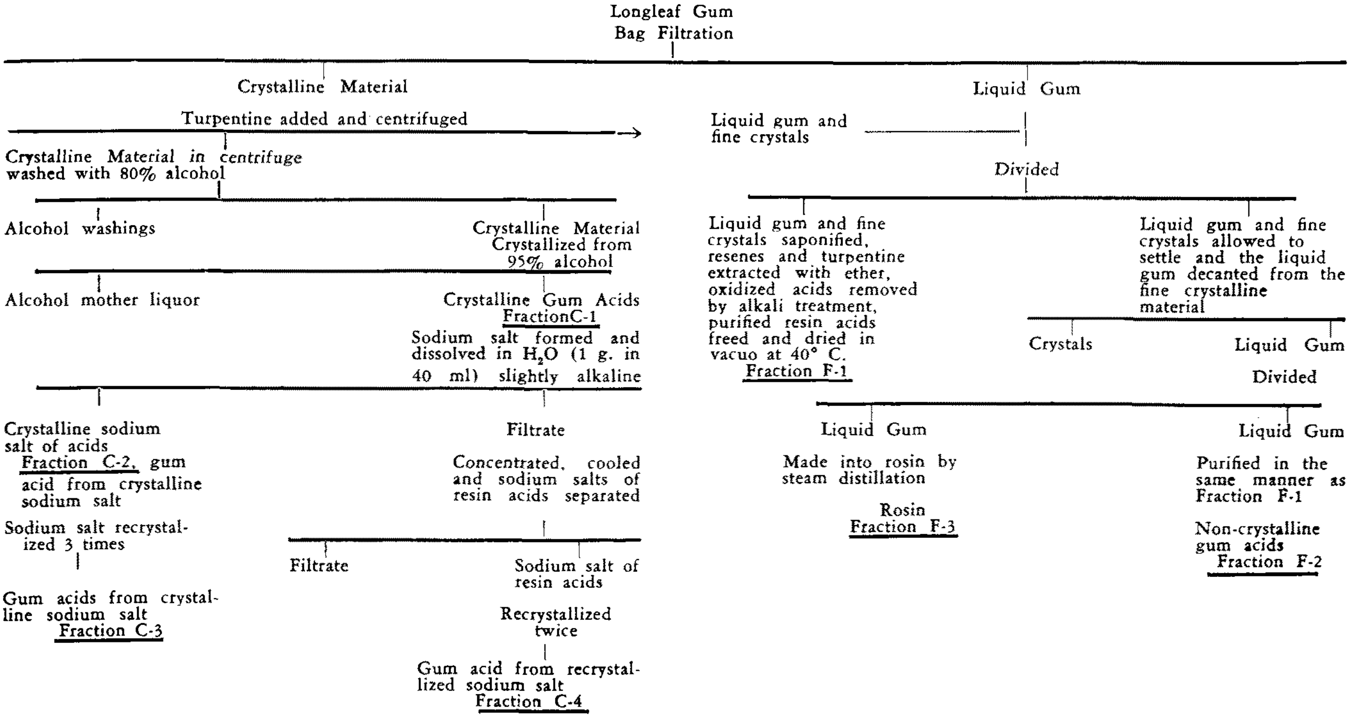
EFFECT PRODUCED BY HEATING AND BY EXPOSING TO AIR IN THE POWDERED STATE FRACTIONS RICH IN CRYSTALLINE GUM ACIDS

	Specific Rotation Before and After Heating		Soap Darkening Index Before and After Heating			Soap Darkening Index Before and After Exposing to Air in the Powdered State		
Fraction	Before	After	Before	After	Color	Before	After	Color
C-1	— 80°	—16°	.27	1.17[1]	orange	.27	1.17	Dark Brown
C-2	—115°	—	.33	1.05[1]	orange	.33	.95	Brown
C-3	— 2°	+40°	.00	.57	yellow	.00	.03	White
C-4	— 2°	—25°	.72	1.00	brown-yellow	.72	.84	Brown

[1] Have color characteristic of soaps made with abietic acid.

FLOW SHEET I

Fractionation of Gum Acids



The crystalline gum acids, Fractions C-1 and C-2 gave light colored rosin soaps, and Fraction C-3 (80 per cent d-pimaric and 20 per cent 1-pimaric) made a white rosin soap. The data in Table II points to the conversion of one or more of the crystalline acids by heat to an abietic type acid. One of the acids converted is undoubtedly 1-pimaric, which Kohler (10) has shown can be isomerized by heat to 1-abietic acid. The color of the rosin soap made from heat-treated Fraction C-1 and C-2 had the same characteristic orange hue as that made with abietic acid. Also, the change in specific rotation of Fraction C-3 when heated was approximately the same as that calculated for the conversion of the 1-pimaric acid present to 1-abietic acid and the darkness index of the rosin soap made from heat-treated Fraction C-3 is approximately the same as that of a rosin soap made with a quantity of abietic acid equal to the 1-pimaric acid in the rosin soap made with Fraction C-3. That 1-pimaric acid was not the only acid affected by heat was indicated by the change in specific rotation of the Fraction C-4 when it was heated, the change in this case was just the opposite of that for 1-pimaric acid and indicated that some acid or acids were converted to a form having a less positive or more negative rotation.

The data in Table II show that at least one of the resin acids present in Fractions C-1, C-2 and C-4 was oxidized under the conditions of the test, but that d- and 1-pimaric acids in Fraction C-3 were not. Later tests indicated that the unstable acid or acids were more closely related to the crystalline than to the non-crystalline gum acids.

Non-Crystalline Gum Acids (Sapinic Acids)

The bag filtrate and liquid gum (containing fine crystals which passed through retaining cloth) from the centrifuge separation were combined and fractionated as shown in Flow Sheet I.

This yielded three fractions. Fraction F-1 contained non-crystalline gum acids together with the resin acids of the fine crystalline material that passed through the centrifuge with the liquid gum. Fraction F-2 was the same as Fraction F-1, except that resin acids of the fine crystalline material were not present. Fraction F-3 was the same as Fraction F-2, except that it contained the resenes and oxidized constituents originally present in the gum. Rosin soaps were prepared from the above fractions both before and after treatment. The data from these experiments are summarized in Table III.

TABLE III.

EFFECT PRODUCED BY HEATING AND BY EXPOSING TO AIR IN THE POWDERED STATE FRACTIONS RICH IN NON-CRYSTALLINE GUM ACIDS

	Soap Darkening Index before and After Heating		Soap Darkening Index Before and After Exposing to Air in the Powdered State	
Fraction	Before	After	Before	After
F-1	.42	.87	.42	1.17
F-2	.43	.78	.43	1.02
F-3	.58	.79	.58	1.02

The data from these experiments indicate that as the crystalline gum acids are removed, the fraction rich in non-crystalline gum acids is affected less by oxidation and heat. This indicates that the acids most sensitive to oxidation and heat (isomerization to abietic type acids) are associated with the crystalline gum acids rather than the non-crystalline gum acids. The presence of resenes does not appear to promote or retard the action of heat or oxygen on the non-crystalline gum acids (Fractions F-2 and F-3).

The resenes were obtained by extracting with ether an aqueous solution of the saponified liquid portion of the gum. The ether and turpentine were removed from the extracted resenes by distillation in vacuum. The test soap cakes were made to contain 5 per cent resene. This was more than twice the resene content of our regular rosin soaps. The soap darkening index of resenes, untreated, exposed in a thin film and heated, was 0.09, 0.12 and 0.08. Under the conditions of our experiment the resenes contributed very little color to rosin soap, and were not affected by oxidation or heat. In this investigation we have no evidence of the resenes either hindering or aiding any of the changes observed.

The abietic acid was prepared by the method of Palkin and Harris (15) and recrystallized until it had a specific rotation of -80° or greater. The freshly prepared abietic acid was used in all tests. The soap darkening index of abietic acid, fresh, exposed in powdered state and heated, is 1.17, 1.20 and 1.17. These test soap cakes had a characteristic orange color that has not been found in any rosin soaps made with gum rosin. At the time of molding, abietic acid soap was as light as any made with rosin but as soon as water was lost, color developed. The darkness index was the same for soap cakes dried by exposure to air or in a desiccator in an atmosphere of nitrogen over $CaCl_2$.

The soap darkening index of abietic acid when the soap cake contains abietic acid and fatty acid in the ratio of 1/24 (instead of the usual ratio of 1/4) was 0.6. The soap cake had a brighter yellow color than the test rosin soap cakes having the same darkness index but made with rosin.

The pyroabietic acid for the following tests was prepared by the method of Fleck and Palkin (6). The soap darkening index of pyroabietic acid, untreated, exposed and heated, was 0.00, 0.05 and 0.03. All of the rosin soap cakes made with pyroabietic acid were white, showing that the treatment given them prior to being incorporated in the soap produced little or no change in the pyroabietic acid that affects the color of the soap.

Table IV summarizes the characteristics of a rosin and of those preparations which can be produced in a relatively pure state.

TABLE IV

EFFECT PRODUCED BY EXPOSING TO AIR IN THE POWDERED STATE AND BY HEATING RESIN AND ROSIN ACIDS AND NORMAL ROSIN

Material	Untreated		Treated			
			Exposed		Heated	
	Soap Darkening Index	Color of Soap Cake	Soap Darkening Index	Color of Soap Cake	Soap Darkening Index	Color of Soap Cake
Resin Acid (80% d-pimaric and 20% 1-pimaric)	0.00	white	0.03	white	.57	yellow
Resenes (soap cake contains 5%)[1]	0.09	yellow tint	0.12	yellow tint	0.08	yellow tint
Abietic Acid	1.17	orange	1.20	orange	1.17	orange
Pyroabietic Acid	0.00	white	0.05	white	0.03	white
Normal Rosin	0.64	yellow-brown	1.17	dark brown	0.74	yellow-brown

[1] Resene content more than twice that present in soap cakes made with normal rosin.

The data in Tables II, III and IV show that two sources of the color a normal rosin contributes to soap are the abietic or abietic type acid and the oxidized rosins and rosin acids. Due to the conversion of certain unstable resin acids by heat some abietic and abietic type compounds will always be present in rosin processed in the usual manner. The amount of oxidized resin and rosin acids in a rosin will vary considerably, depending upon the manner and time the gum or rosin is exposed to air. Both the soap darkening index of normal rosin and the color of the soap cake indicate that *normal* rosin is by no means 90 per cent abietic acid as some authors assume.

The Color Contributed to Soap by Rosins and Laboratory Modified Rosins

The large number of factors that might be responsible for variable results obtained with commercial rosins of the same grade when used in soap makes it necessary to know, for each rosin tested, the origin of the gum from which it is made, how the gum was collected, and how the gum was treated prior to and including distillation. When suitable commercial rosins could not be obtained, such rosins were produced in the laboratory from specially collected gums under carefully controlled conditions.

Rosins were available for comparing the effect of specie-longleaf and slash pine gum, rosins from uncleaned and cleaned gum, rosins from gum distilled on steam and fire stills, rosins from gums collected early and late in the season, rosins from gums low (estimated to contain 20 per cent or less scrape) and high in scrape (20 to 100 per cent scrape) and effect of cups. Of these factors only one, the presence of scrape in the gum, showed an appreciable effect on the color contributed to soap by rosin. (See Table V).

TABLE V.
EFFECT OF SCRAPE ON THE SOAP DARKENING INDEX OF THE ROSIN

Rosins from Gum Low in Scrape		Rosins from Gum High in Scrape	
Soap Darkening Index of Rosin	Grade of Rosin	Soap Darkening Index of Rosin	Grade of Rosin
.50	WW	.75	WW
.57	WG	.77	K
.70	WW	1.00	N
.74	WG	1.00	I
.62	X	1.10	M

The extent of oxidation of the scrape is a factor but can only be estimated. Rosins made from older and more oxidized scrape give more brown color to rosin soap than those made with fresher and less oxidized scrape.

Effect of Resinates, Cups, Length of Face and Temperature of Distillation

The presence of metallic compounds formed by the action of the gum or the water in the gum on metal cups used for collection is another factor to be considered. Samples of rosin for comparing the action of the iron, aluminum and zinc resinates were prepared in the laboratory by adding approximately equivalent amounts of the resinates to a high grade slash gum which was then made into rosin. Gums from longleaf and slash pine, collected in raised clay cups and raised and unraised old galvanized iron cups were distilled in the laboratory and the rosins tested. The results of these tests are given in Table VI, and show that zinc (0.13 per cent) and aluminum (0.07 per cent) in the form of the resinate have little effect on the grade of rosin, while iron (0.13 per cent) in the form of resinate has a marked effect. The addition of these resinates to high grade slash gum (in the quantities used) does not affect the color the resulting rosin gives to soap. The raised old galvanized cups have an effect on the grade of rosin, but little effect on the color the rosin contributes to soap. If the old galvanized cups are unraised the grade of rosin is further reduced, and there was an appreciable increase in the color given to the soap by the rosin. The color of the rosin soap indicates that it is due to oxidized resin acids which are formed to a greater extent when the gum has to pass over a long face to the cup. The tests also indicate that longleaf gum collected in old galvanized cups makes lower grade rosin than slash gum collected in the same manner.

TABLE VI.
EFFECT OF RESINATES, CUPS AND LENGTH OF FACE

Gum	Grade of Rosin	Soap Darkening Index of Rosin
High slash content	X	.63
High slash + Zn resinate	X	.62
High slash + Al resinate	WW	.57
High slash + Fe resinate	D	.62
Longleaf gum collected in raised clay cups (face 14")	X	.58
Slash gum collected in raised clay cups (face 14")	WW	.58
Longleaf gum collected in raised old galvanized cups (face 14")	H	.68
Slash gum collected in raised old galvanized cups (face 14")	N	.63
Longleaf gum collected in unraised old galvanized cups (face 54")	B	.86
Slash gum collected in unraised old galvanized cups (face 54")	H	.80

Pine bark was added to the gums distilled in the laboratory. There was no sticking of the bark to the walls of the flask during distillation, and the temperature of the walls never exceeded 200° C. and the gum 170° C. Under these conditions the added bark had no effect on the color the rosin contributes to soap.

The temperature to which the gum is subject may vary, according to the procedure of distillation. To test the effect of temperature, three types of gum were steam distilled in the laboratory to yield rosins with normal turpentine content. One rosin of each type was subjected to additional heat treatment (180° C. for 5 hours) in a sealed tube. The results are given in Table VII.

TABLE VII.
Effect of Temperature to which Gum Has Been Subjected During Distillation.

Type of Gum	Temp. of Oil Bath °C.	Maximum Temp. of Gum °C.	Grade of Rosin	Soap Darkening Index of Rosin	Soap Darkening Index of Rosin Heated 5 Hrs. at 180° C. in Sealed Tube
Slash	160	135	2A+	.55	
Slash	200	170	X	.61	.64
Longleaf	160	135	N	.63	
Longleaf	200	170	M+	.65	.74
Scrape	160	135	N+	.87	
Scrape	200	170	M	.85	.85

Note: Usual turn out temperature at gum still is 160°-165° C.

The temperature used in these experiments had little or no very marked effect on the color the rosin gives to soap. It is interesting to note that the temperature to which scrape is heated during distillation had an appreciable effect on the grade of rosin, but no effect on the color which the rosin gives to soap. The effect of additional heat on the color contributed to soap by rosin from longleaf gum may be explained by the more complete conversion of certain crystalline type acids (of which longleaf gum appears to have more than slash) to abietic type acids.

Vacuum Distilled Rosin

A WW rosin made from slash gum collected in raised clay cups was distilled at 200° to 250° C. at a pressure of 1 to 4 mm. of mercury. The rosin obtained by this means graded 3A and had an acid number of 165. The soap darkening index of this 3A rosin was .74, and after being exposed to air for one week in powdered form, was 1.24. Both of these values are approximately the same as those for the original WW rosin before and after exposure. The color of the rosin soap made with the unexposed 3A rosin resembled the rosin soaps made with abietic acid but the color of the rosin soaps made with the 3A rosin after being exposed to air for one week in the powdered state was more like that of soap made with normal rosin treated in a similar manner. These tests indicate: That the abietic type acids in the rosin are distilled in vacuuo; that the oxidized compounds are left behind or are converted to some other form; that the distilled product is as sensitive to oxidation as the original gum rosin; and that from the standpoint of color contributes to soap, a vacuum distilled gum rosin is not likely to have much advantage over a clean, high grade gum rosin.

Rosin from Oxalic Acid Treated Rosin and Gum

Another factor is the effect of oxalic acid on gum and rosin. Oxalic acid has been used to remove iron from the gum or to reduce the color given to rosin by iron compounds present. The effect of oxalic acid on high grade slash gum and rosin, high grade slash gum to which iron resinate had been added, a longleaf gum collected in old galvanized cups, and a commercially treated rosin, was tested. The results are given in Table VIII.

TABLE VIII.

Effect of Oxalic Acid Treatment

Test No.	Type of Gum[1]	Treatment of Gum or Rosin	Grade of Rosin	Soap Darkening Index of Rosin
1	High grade slash	—	X	.55
2	Same as No. 1	a[2]	N	.82
3	Same as No. 1	b[3]	X	.52
4	Same as No. 1	c[4]	WG	.92
5	Same as No. 1 + Fe resinate	—	D	.61
6	Same as No. 5	a	K	.92
7	Same as No. 5	b	N—	.52
8	Longleaf gum collected in clay cups	—	N	.62
9	Similar to No. 8, but collected in old galvanized cups	—	B	.82
10	Same as No. 9	b	N—	.67
11	Sample of untreated commercial rosin	—	I	.98
12	Sample of treated commercial rosin made from same gum used in 11	[5]	I	1.15

[1] 400 gm. gum used for all laboratory prepared rosins.

[2] (a) 2 gm. oxalic acid added to the gum and the gum distilled.

[3] (b) Gum warmed to 95° C., shaken with 5 per cent water solution of oxalic acid until iron had reacted, diluted with fresh turpentine, the aqueous phase allowed to separate and the gum decanted, filtered and distilled.

[4] (c) Oxalic acid stirred into hot rosin just after pouring from distillation flask.

[5] Oxalic acid added to rosin in still.

The first four tests show the effect of different methods of oxalic acid treatment on high-grade gum and rosin. The color of rosin soaps in tests 2, 4 and 6 is similar to that of rosin soap made with abietic or abietic type acids. Therefore, we believe that the darker color of these rosin soaps comes from abietic type acids produced by the isomerizing action of oxalic acid. Under the conditions of procedure (b) oxalic acid treatment does not affect the color of the rosin soap, test 3.

Experiments in this laboratory indicate that iron resinate added to a high grade gum does not contribute noticeably to the color of the rosin soap until its concentration is sufficient to reduce the grade of rosin to E or lower. The removal of iron resinate from gum by procedure (b), we believe, accounts for the improvement in color of the rosin soaps of tests 7 and 10.

All of the tests made indicate that procedure (b) is superior to (a) and (c), having little or no effect on the unstable resin acids (as indicated by the soap darkening index of the rosin), and improves the grade of rosin if the iron content of the gum is high enough to appreciably discolor the rosin when processed in the usual manner.

Effect of Aging of Soap Cakes on Their Darkness Index

The darkness index of a series of laboratory test soap cakes one month old and 7 months old are given in Table IX.

TABLE IX

Changes in Darkness Index of Rosin Soap Cakes during Aging.

Acids or fractions used to prepare rosin soaps	Darkness Index — log B 3 to 5 wks. after molding	Darkness Index — log B 7 months after molding	Difference
Blank (white soap stock)	0.40	0.44	+0.04
Pyroabietic Acid	0.42	0.54	+0.12
5 per cent resene soap	0.46	0.66	+0.20
Oxidized abietic acid	1.53	1.52	—0.01
Oxidized crystalline gum acids, Fraction C-1, Table II	1.57	1.51	—0.06
Oxidized non-crystalline gum acids, Fraction F-1, Table III	1.57	1.51	—0.06
Oxidized Rosin	1.57	1.55	—0.02
Abietic Acid	1.51	1.45	—0.06
Heat Treated crystalline gum acids Fraction C-1, Table II	1.57	1.55	—0.02
Heat Treated non-crystalline gum acids, Fraction F-1, Table III	1.28	1.28	0.0
Untreated crystalline gum acids, Fraction C-1, Table II	0.67	1.16	+0.49
Untreated non-crystalline gum acids, Fraction F-1, Table III	0.83	1.26	+0.43
Untreated Fraction C-3, Table II (80% d- and 20% l-pimaric acid)	0.40	0.78[1]	+0.38
Normal high grade rosin	0.96	1.20	+0.24

[1] After 3 months.

The only rosin soaps that did not show an appreciable change in darkness index were those dark in color when one month old and the one made with pyroabietic acid. The former have such a low blue reflectance that only a marked increase in the colored compounds present would have produced a change in the darkness index. The fact that the soap cake made with pyroabietic acid did not change appreciably with age indicates that it was more stable than the other products that yielded medium and light colored rosin soaps.

Summary

A method has been described for evaluating the darkening a rosin will impart to soap. This method involves the preparation of a rosin soap and measuring its reflectance relative to MgO for blue light, wave length 436 mu with a photo-electric photometer. The color contributed to a soap by rosin has been evaluated by the soap darkening index of the rosin (-log B for the rosin soap less -log B for the soap stock).

The primary gum acids in their original states contribute little or no color to rosin soaps, but some of them are so unstable toward heat and oxygen that color producing acids are always found in rosins made from gum collected and processed in the usual manner. The amount of these color producing acids present depends upon type of gum, conditions of collection, and processing. The tests indicate that the acids most unstable to heat and oxygen are associated with the resin acids that crystallize readily from the gum, rather than with those that do not, and that the resenes are stable toward heat and exposure and do not aid or hinder any of the changes observed.

Abietic and abietic type acids give a characteristic orange color to rosin soap cakes prepared by the method adopted. Soap tests confirm the findings that some of the crystalline type rosin acids are converted to abietic type acids when heated. The darkness index and the color of the rosin soap cake made with normal gum rosin both indicate that normal gum rosin is not 90 per cent abietic acid, as some suppose.

It has been shown that the resinates of iron, aluminum and zinc are negligible factors in contributing to the color of rosin soap and that the presence of scrape or oxidized resin and rosin acids increase the color rosin gives to soap.

Use of oxalic acid in the gum during distillation favors the production of acids that give color to soap and the color of the soap indicates that they are an abietic type acid. It has been shown that iron contaminated gum can be treated with oxalic acid without isomerizing the primary acids to forms that give color to soap.

Aging tests showed that, after the first month the rosin soap cakes changed color slowly. The change that took place in the following months involves an appreciable darkening of the lighter samples, except in the case of the white rosin soap made with pyroabietic acid.

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A Crystallization Method for the Determination of Saturated Fatty Acids in Soybean Oil

By F. R. EARLE and R. T. MILNER

U. S. REGIONAL SOYBEAN INDUSTRIAL PRODUCTS LABORATORY, URBANA, ILLINOIS.[1]

THE American Oil Chemists' Society has adopted two official methods (6) for the determination of the amount of saturated acids in vegetable and animal oils and fats, namely, the thiocyanogen and the modified Twitchell lead salt-alcohol methods. The thiocyanogen method is applicable only to those oils which do not contain linolenic acid and therefore cannot be used with the drying oils and a few of the semidrying oils. The modified Twitchell method is probably the most generally used procedure for determining saturated acids, although the data presented at the time of its adoption as a tentative method (3) showed that the results obtained with it were from 0.9 to 2.0 percent lower than those calculated by the thiocyanogen method. This discrepancy had been noted previously by Martin and Stillman (5) who suggested that the results of the thiocyanogen method were probably more nearly correct. Aside from the question of the accuracy of the results, the manipulation involved in a lead salt separation is so tedious and time consuming that the method is not well adapted to routine determinations.

In addition to these official methods, there are a number of procedures involving oxidation of the unsaturated compounds with potassium permanganate and isolation of the unaltered saturated acids. Probably the best known of these methods is that devised by Bertram (1) which is said to be more accurate (4) than the Twitchell method, but it is also more tedious.

In preparing linoleic acid by crystallization at low temperatures, Brown (2) observed that the saturated acids could be separated from the unsaturated acids in acetone at -20° C. with an efficiency at least equal to that of the Twitchell method. This observation led the present authors to the development of a crystallization method for determining the saturated acids present in soybean oil. The determination can be made in a short time with simple equipment. During the developmental stages, the apparatus used consisted of a number of 38 by 200 mm test tubes, a 30-mm glass filter stick of G3 porosity, and a two-quart vacuum food jar to contain the low temperature acetone bath. The temperature was controlled by the addition of dry ice as required. A larger bath with automatic temperature control would be highly desirable for any long series of determinations.

Method

The mixed fatty acids are prepared from the oil according to the present official method of the American Oil Chemists' Society (6).

A sample of about 5 g of mixed acids is placed in a test tube, and 50 ml of acetone is added. The tube and its contents are suspended in a cold bath consisting of acetone and dry ice at about -41° C., and the sample is stirred occasionally with a thermometer until the temperature reaches -40° C. The soluble acids are then removed by filtering through a glass filter stick which has been previously cooled to the temperature of the bath. The solid materials clinging to the thermometer and filter stick are washed back into the test tube with 50 ml of acetone and permitted to dissolve. After two more crystallizations the solid acids are dissolved in acetone and transferred to a small tared flask. The solvent is removed on a steam bath, and the residue is dried in an oven at 105° C. for one-half hour. The flask and contents are cooled and weighed, and the amount of "solid" acids is calculated. The iodine number of the "solid" acids is determined and used to calculate the amount of unsaturated acid in the "solid" acid fraction, assuming that the only unsaturated acid present is oleic. Subtraction of the "oleic" acid from the "solid" acids gives the amount of saturated acids present in the original sample of mixed fatty acids.

Discussion

In the study of soybean oils, it was found that working at a temperature of -40° C. permitted a sharp separation of the unsaturated acids from the saturated acids and at the same time gave excellent recovery of the saturated acids. The solubilities of stearic, palmitic, and myristic acids in acetone at -40° C. were found to be approximately 1, 8, and 75 mg per 100 ml, respectively. Losses of this magnitude were not considered to be serious in the case of stearic and palmitic acids, and, in the case of myristic acid, the loss is probably no more serious than those which occur in the Twitchell and oxidation methods. The solubility of the saturated acids in acetone solutions of the unsaturated acids was not studied. The work on soy-

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