tion of the unsaturated linkages in the chain, is not evident. The latter would seem to be the more tenable conclusion.

Bibliography

1. Lebedeff, A. Pflüger's, Arch. ges. Physiol., **31**. 11 (1883).
2. Rosenfeld, G., Z. klin. Med., **36**, 232 (1889); Ergebnisse Physiol., **1**, 651 (1902).
3. Leathes, J. B., and Wedell, L. M., J. Physiol., **38**. Proc. 38–40 (1909).
4. Hartley, P., J. Physiol., **36**, 17 (1907); ibid., **38**, 353 (1909).
5. Leathes, J. B., Harvey Lectures (1908–09), p. 213.
6. Joannovics, G., and Pick, E. P., Wien. klin. Wochschr., **23**, 573 (1910).
7. Imrie, C. G., J. Path. Bact., **19**, 245 (1914).
8. Burr, G. O., Burr, M. M., and Miller, E. S., J. Biol. Chem., **97**, 1 (1932).
9. Turner, K., Biochem. J., **24**, 1327 (1930).
10. Channon, H. J., Irving, E., and Smith, J. A. B., Biochem. J., **28**, 840 (1934).
11. Tsujimoto, M., Chem. Umschu. Fette, Ole, Wachse, Harze, **32**, 125 (1925).
12. Wesson, L. G., J. Biol. Chem., **65**, 235 (1925).
13. Müller, P., Arch. exptl. Path. Pharmakol., **147**, 219 (1930).
14. Bloor, W. R., J. Biol. Chem., **80**, 443 (1928).
15. Bloor, W. R., and Snider, R. H., J. Biol. Chem., **87**, 399 (1930); ibid., **99**, 555 (1933).
16. Brown, J. B., J. Biol. Chem., **80**, 455 (1928).
17. Brown, J. B., and Ault, W. C., J. Biol. Chem., **89**, 167 (1930).
18. Klenk, E., and Schönebeck, O., Z. physiol. Chem., **209**, 112 (1932).
19. Brown, J. B., J. Biol. Chem., **97**, 103 (1932).
20. Sinclair, R. G., J. Biol. Chem., **96**, 103 (1932).
21. Berend, N., Biochem. Z., **260**, 490 (1933).

A GENERAL COMPARISON OF THE PROPERTIES OF PALE WOOD AND GUM ROSINS*

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This is a rather non-technical paper, discussing briefly how wood rosin is made and comparing the chemical properties of Pale Wood Rosins to those of the Pale Gum Rosins, a raw material with which all soap manufacturers are familiar.

Gum rosin has been produced in this country for centuries, and since its inception, the soap industry has been one of the principal consumers of this raw material. In view of the age of the industry and the importance of the raw material to the soap chemist, it is not surprising that you well understand the physical and chemical properties of gum rosin and the part it plays in the production of good soap.

In the year 1910, the first large unit of a new industry was completed, based on research that had been carried on for many years previous to that date. In that year wood rosin, made by the steam and solvent process, was produced commercially by Homer T. Yaryan. From the beginning the process and industry was destined to be successful, and thus in twenty-four years has grown to be a major factor in the Naval Stores world. In 1933, the production of all grades of wood rosin reached 226,500,000 pounds, or approximately 23 per cent of the total production of rosin in the United States. All manufacturers are vitally interested in all sources of supply of the raw materials they use and so it is not surprising that the soap industry has become interested in wood rosin. We hope that what we have to say about wood rosin in the following paragraphs will help you to better understand this soap-making raw material.

Wood rosin is produced by the steam and solvent process from the oleoresin in Southern long-leaf and slash pine stump wood. This is the same type of oleoresin from which gum rosin is produced. The gum rosin producer bleeds the oleoresin from the living tree. When the tree is cut down, the stump, rich in oleoresin, is available to the wood rosin producer as a raw material from which to make his rosin. So we point out that both gum and wood rosins come from the same natural source.

The first step in the production of wood rosin is the pulling of the stumps, grading, and shipping them into the plant. Only highly productive wood is used. At the plant the wood is put through chippers, where it is comminuted into small chips and is so prepared for the process.

This wood is charged into large vertical digesters and first exposed to steam. The steam passes through the wood chips, volatilizing the greater portion of the volatile oils, such as turpentine and pine oil, and carries them off to condensers where they are recovered. After the volatile oils are removed, the steam is turned off and a hot solvent turned into the digesters. This hot solvent dissolves out all of the rosin and the remainder of the oils and carries them into evaporators where the solvent and oils are evaporated off and the rosin obtained. The rosin as it comes from the evaporators is generally dark ruby red in color and known as an FF grade of rosin. FF Wood Rosin can be further processed to pale grades of rosin by selective solvent or other types of refining to remove color bodies.

The soap industry consumes principally the medium pale grades of rosins, such as I and M Rosins. There is comparatively little rosin as dark as F Rosin used and comparatively small quantities of grades as light as WG or WW going into the soap kettle. In view of this, we will confine the comparison of wood and gum rosin to the most widely used pale grades, such as I and M grades of rosin.

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As previously stated, both wood and gum rosins come from the same natural source, and, therefore, you would expect them to be similar products. Both pale gum and wood rosins generally contain approximately 90 per cent resin acids reported to consist mainly of abietic acid and isomers of abietic acid having the formula $C_{20}H_{30}O_2$.

The remaining 10 per cent is reported to consist chiefly of volatile and non-volatile resenes, along with saponifiable esters and other saponifiable material.

A good average typical analysis of both pale wood and gum rosin serves very well to compare the two products. Such a typical analysis generally includes determination of color, acid number, saponification number, melting point, unsaponifiable, petroleum ether insoluble, and toluene insoluble. We quote as follows an average typical analysis of I and M wood Rosins, in comparison to an average typical analysis of the same grades of gum rosins.

	I Wood	I Gum	M Wood	M Gum
Color	I	I	M	M
Melting point (drop)	176° F.	180° F.	176° F.	179° F.
Acid number	166	166	167	165
Saponification No.	171	175	172	176
Unsaponifiable	7%	6.5%	7%	7.5%
Pet. ether insol.	0.15%	2.5%	0.15%	2.5%
Toluene insoluble	0.003%	0.09%	0.002%	0.07%

The wood rosin samples for these average analyses were taken from our regular plant production and the gum rosin analyses were obtained from a reliable Government source. Realizing that rosin is not a chemically pure product, it is evident that these values will vary between certain limits. By virtue of the method by which wood rosin is made, better chamical control is possible and as a result wood rosin is the more uniform product. The analytical constants of gum rosins as a rule vary over wider limits than do those of Pale Wood Rosins. For the purpose of comparison, it is necessary that we use average analyses taken as an average of the large number of samples. The analyses which we have quoted serve very well to compare these two types of rosins made by different processes and to show general trends regarding any differences between them. We shall take each determination separately and discuss any differences.

The first quoted in the analysis is a determination of color. The color of both pale wood and gum rosins, grade for grade, is the same. Government standards dictate the classification of rosin as regards color and, therefore, the two types of rosins must be of approximately the same color to be sold as the same grade. The producers of wood rosins are constantly on the alert to control the color of their product and give the rosin consuming industry a very uniform product year in and year out. The soapmaker is, of course, interested in the color of his rosin and he can purchase any color or grade to meet his specifications. At most, the variance in color between one shipment and another of either gum or wood rosin is very small and, therefore, of little concern to the soap-maker. However, the hue of color of Pale Wood Rosin is not the same as the hue of Pale Gum Rosin. The wood rosin has a more pronounced and brighter yellowish hue. This same difference in hue is observed in soap made from the rosins. The hue of I Wood Rosin Soap is brighter and more on the yellow than that of I Gum Rosin Soap, which has more of a greyish tinge. Soap made from Pale Wood Rosin in general has a brighter color than similar soap made from Pale Gum Rosin.

The second analysis reported is that of melting point. Here there is a slight difference between wood rosin and gum rosin. From the analyses reported, I Wood Rosin has an average melting point 4° lower than I Gum Rosin, while M grade shows the average melting point of the wood rosin to be 3° lower than the gum. So we say that in general wood rosins have a slightly lower melting point, grade for grade, than gum rosin.

The melting points of the various resin acids in rosin, as pure organic acids, are constant. Therefore, apparently, the remaining constituents of the rosin are the chief factors controlling the melting point.

We know that variations in the content of resenes and volatile oils greatly influence the melting point of any grade of rosin. The volatile oil content of Pale Wood Rosins will average only about 0.15%, which is much lower than is found in similar grades of gum rosin. Because the volatile oil content in Pale Wood Rosins is lower than in corresponding grades of gum rosins, it does not appear that the slightly lower melting point of wood rosins is due chiefly to volatile oil content.

As far as we have been able to determine, the resenes found in wood rosins are apparently of a softer nature than those found in gum rosins, and thus we believe that the lower melting point of wood rosins is due chiefly to the presence of softer resenes in the wood rosin.

The melting points of both wood and gum rosins vary within limits. These slight variations in the melting point of any given grade of rosin apparently do not affect the soap-maker's finished product, so it appears that wood rosin and gum rosin, as far as the soap-maker is concerned, are on a par in regards to melting point.

The next analysis to consider is that of acid number. The acid number of a rosin measures the content of free resin acids present in any particular grade of rosin. The exact components of the free resin acids in any rosin and their percentage composition in the rosin is still the subject of much discussion. E. A. Georgi*, in a paper presented before a meeting of the American Association for the Advancement of Science, points out that pure research on rosin acids has been conducted for over one hundred years. This research has led to the discovery that several isomeric acids exist and that others can be artificially created by isomerization. These different acids or isomers can be identified by their crystal forms, melting point, and optical rotation. However, because of the often peculiar action and transitory nature of some of these acids, which was not always known to the early workers in this field, many of the properties determined and recorded by them are of little value. At present the literature lists some thirty odd crystalline rosin acids, not to mention the references to non-crystalline acids. In this same paper, Georgi lists a few of the more important rosin acids which have been isolated. Most of these that are present in rosin are isomers of abietic acid, and, therefore, for all practical purposes we may consider that the formula for the rosin acids contained in rosin is $C_{20}H_{30}O_2$.

A certain percentage of acetic acid can be obtained from heart-

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wood of pine trees, and undoubtedly, in the presence of this acid in the wood, and aided by the heat of the sun, there is a partial isomerization of the natural acids in the tree. In view of the fact that wood rosins are made from the oleoresin in stump wood which is always exposed to the heat of the sun for many years longer than the oleoresin from which gum rosin is made, it is reasonable to believe that wood rosins will contain larger quantities of isomerized or abietic acid than the gum rosins which contain mainly the natural primary acids. This theory is more or less confirmed when we compare the optical rotation of gum and wood rosin. In general, the Pale Wood Rosins have an optical rotation very close to zero or very slightly on the dextro side, whereas most of the Pale Gum Rosins have specific rotations very decidedly on the dextro side and run as high as + 30 or 35°. Further, pure abietic acid does not react with hydrated lime at any temperature up to about 500° F. By studying the reaction of hydrated lime with wood rosin and gum rosin, we find that Pale Wood Rosin is generally less reactive. The reason for this lack of reactivity with hydrated lime is given by explaining that the free resin acids in wood rosin contain higher percentages of abietic acid than those in gum rosin. Also, in studying the selective solvent purification of wood rosin, we find that its composition approaches that of pure abietic acid. In view of these studies, we feel fairly safe in stating that in general the Pale Wood Rosins contain more of the isomer, abietic acid, than do the Pale Gum Rosins.

Pure abietic acid and potassium hydroxide in aqueous solution react to form potassium abietate according to the formula: $C_{20}H_{30}O_2 + KOH + Aq$ gives $C_{19}H_{29}COOK + H_2O + Aq$. As previously stated, we may consider for all practical purposes that the chemical formula of the resin acids present in both wood and gum rosin is $C_{20}H_{30}O_2$. The molecular weight of resin acids having this formula is 302.34, and that of potassium hydroxide is 56.11, and therefore, we can calculate from the above equation the acid number of the pure resin acids as 185.6. Knowing the acid number of these pure resin acids and the acid number of any rosin, we can then calculate the total per cent free resin acids present in the rosin. Going back to the analysis of the Pale wood and gum rosins, we note that the I Wood Rosin has an acid number of 166, and dividing this by 185.6, we determine that this grade of Pale Wood Rosin contains approximately 89.4% free resin acid. The I Gum Rosin with an acid number of 166 contains, then, 89.4% free resin acid. M Wood Rosin with an acid number of 167 contains 90%, and M Gum Rosin with an acid number of 165 contains 89%. Comparing these percentages of free resin acids present in wood and gum rosins, we find the I grade of wood and gum rosin to be the same, while in the M grade the wood rosin contains about 1% more. However, before drawing any conclusions from these figures, we must consider the degree of accuracy of the acid number determination. In rosins having an acid number of about 165, such as these we are discussing, the method is accurate to approximately plus or minus 0.5%. Taking this into account, and remembering that the acid number of wood and gum rosins will vary over a narrow range, it would be splitting hairs to attempt to state that gum or wood rosins, grade for grade, contain the most free resin acids.

The next analysis to consider and compare is that of saponification number. In this respect we find saponification numbers of 171 for the I Wood Rosin, 172 for the M Wood Rosin, and the gum rosins with 175 for the I grade and 176 for the M grade. From these figures we see that the saponification values of Pale Wood Rosin are slightly lower than those of comparable grades of gum rosin, the average being about four points lower. So in general we say that wood rosins have very slightly lower saponification numbers.

The saponification number is reported as the number of milligrams of potassium hydroxide required to neutralize the resin acid and saponify the saponifiable esters in one gram of rosin. The acid number reports the quantity of potassium hydroxide required to neutralize the free resin acids, so the difference between acid number and saponification number indicates the quantity of potassium hydroxide required to saponify the saponifiable esters and other saponifiable material. These saponifiable esters and other saponifiable materials are of minor importance compared to the per cent of free rosin acids present. We have previously shown where the free resin acid content of these pale grades of rosins is approximately 89%. From the quoted average analyses of the two grades of gum and wood rosin, we find that the unsaponifiable content averages about 7%. Adding, then, these two figures of 89% resin acid and 7% unsaponifiable, we account for a total of approximately 96% of the rosin, leaving only about 4% to indicate the quantity of saponifiable esters and other saponifiable material present. Compared to the free resin acids, these esters are apparently difficult to saponify, which belief is somewhat confirmed when the methods of analysis are studied. To determine acid number or, in other words, to neutralize the free resin acids present in any rosin, it is necessary only to dissolve the rosin in alcohol and titrate directly with one-half normal alcoholic potassium hydroxide, but to go beyond this and saponify the saponifiable esters, as is done in determining the saponification number, it is necessary to boil an alcoholic solution of the rosin for one hour in the presence of excess alkali. What we learn from studying the methods of analysis, teaches us that free resin acids and alkali react very readily, while the saponifiable esters in rosin react with more difficulty.

Due to the extremely low percentage of saponifiable esters present in pale rosins and the apparent difficulty with which they are saponified, it appears that even though the saponification number of wood rosins is very slightly lower than gum rosin, the difference is not large enough to be of importance when rosin is considered as a soap-making raw material.

The analysis reporting unsaponifiable content appears next. The unsaponifiable content of both gum and wood rosin consists of non-volatile and volatile materials. From the analysis quoted earlier in the paper for comparison, we find wood rosin and gum rosin on a par in respect to quantity of constituents of these two rosins that are completely and definitely unsaponifiable. The values as reported are average values. Unfortunately, the unsaponifiable content cannot be held constant even with the chemical controls possible in making wood rosin. In view of this, the unsaponifiable content will vary slightly, and in order to get a true picture of the unsaponifiable matter in any rosin, it is imperative that a great number of samples be taken and the values averaged. Many soap-makers who knew wood rosin when the industry first started, still stick to the belief that wood rosin contains more unsaponifiable than gum rosin. This is not the case today when refined pale rosins are being considered. As previously stated, the wood rosin producer has been constantly alert to reduce the volatile oil content of his pale rosins and has been successful in reaching his goal. Our pale rosins contain only about 0.15% volatile oils, which is much less than the volatile oil content found in gum rosin. By reducing the volatile oil content of Pale Wood Rosin to a minimum in present day production, Pale Wood Rosins are produced on a par with Pale Gum Rosin in respect to unsaponifiable matter.

The next analysis in line is that of petroleum ether insoluble. Oxidized resin acids are insoluble in petroleum ether, so this determination might better be termed oxidized resin acid content. No doubt many soap manufacturers do not include this determination in their analysis of rosin. If such is the case, we recommend that they give this determination some consideration, because we believe that it is of some importance to them. Oxidized resin acids are much darker in color than the unoxidized resin acids, and when saponified, these oxidized materials produce a very dark colored soap. Therefore, any appreciable amount of oxidized resin acids in a rosin might very easily affect the final color of the soap made from such rosin. Further, the detergent efficiency of soap made from oxidized rosin as compared to soap made from fresh rosin, may be questioned.

From the comparative analyses it is evident that Pale Wood Rosins contain much less oxidized resin acids than the corresponding grades of gum rosin. The Pale Wood Rosins average from 0.1% to 0.15% oxidized resin acid, whereas the gum rosins contain from 1% to 3%. From the standpoint of oxidized rosin, Pale Wood Rosins are superior to Pale Gum Rosins, when the two raw materials are considered for the manufacture of soap.

The last analysis appears as the determination for the per cent dirt present in rosin. This is determined as the per cent of toluene insoluble material in both gum and wood rosins. From the analyses we find the Pale Gum Rosins averaging about 0.1% dirt, whereas the Pale Wood Rosins average about .003%.

Because of the method by which wood rosin is produced in large chemically controlled plant processes, the presence of dirt is definitely eliminated. Because of the absence of dirt and foreign materials in wood rosin, the soap-maker is able to minimize the presence of dirt in his product. This is an important property of wood rosin and one that should appeal to most of the rosin consuming industries. In this respect we state that wood rosins are superior to gum rosins as soap making raw materials.

In summarizing this comparison of pale wood and gum rosins, we find that: (1) the original color, grade for grade, of both pale gum and wood rosins is approximately the same; however, soap made from Pale Wood Rosin has a bright yellow color, whereas soap made from Pale Gum Rosin has a grey-yellow color. (2) The melting points of wood rosins in general are very slightly lower than the corresponding grades of gum rosin. (3) The acid number of wood and gum rosins, grade for grade, is about the same, indicating the same percentage content of free resin acids, but in general this free resin acid content consists of more abietic acid in wood rosin than in gum. (4) The saponification number of Pale Wood Rosins is very slightly lower than the same grade of gum rosin and the difference, in view of methods of analysis and methods of processing rosin in soap formulas, is too small to be of much importance to the soap manufacturer. (5) The unsaponifiable content of both pale gum and wood rosins on an average is the same. (6) Pale Wood Rosins contain much less oxidized resin acids than do Pale Gum Rosins. (7) Wood rosins contain less dirt or foreign materials than gum rosin. (8) The chemical constants of Pale Wood Rosins vary over narrower limits than gum rosins, and, therefore, the wood rosins will run more uniform.

REPORT OF UNIFORM METHODS COMMITTEE**

By J. J. VOLLERTSEN*
Chairman

"The report of the Uniform Methods Committee is going to be very short this morning. There were only two or three reports that came in that required any action, so I will give you our recommendations and, as is the custom, we will have to act upon them to make them a part of our methods.

You heard yesterday the report of the Fat Analysis Committee. This report covered, really, a great deal about their future work and what they intended to do. There was only one change that they recommended in the method as written in our book or in our methods, and that was with reference to the correction of the unsaponifiable matter for the amount of free fatty acids combined therein. They recommended that this particular part of the method be changed to conform with the same method of the Soap Analysis Committee. The Uniform Methods Committee approves this recommendation, and I move, Mr. President, that it be adopted by the Society."

. . . The motion was seconded, voted upon, and carried . . .

"The Soap Committee had two recommendations, which they brought in with their report. The first was that the Wolff's Method, modified, is not detailed enough to follow. They recommend, therefore, that the method be re-written and clarified without changing any of the fundamentals. The Uniform Methods Committee approves this, and I move, Mr. Chairman, that it be changed and that it remain as a tentative method for another year."

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*Armour & Company, Chicago.

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