differences within each class. It is not known why this is so.

The absence of any relationship between the various tests applied to oil immediately after bleaching is evidence of selective adsorption. It might be possible to deduce from this that the adsorbents which give poor induction periods are selectively adsorbing stabilizing bodies that are not measured by any of the existing tests.

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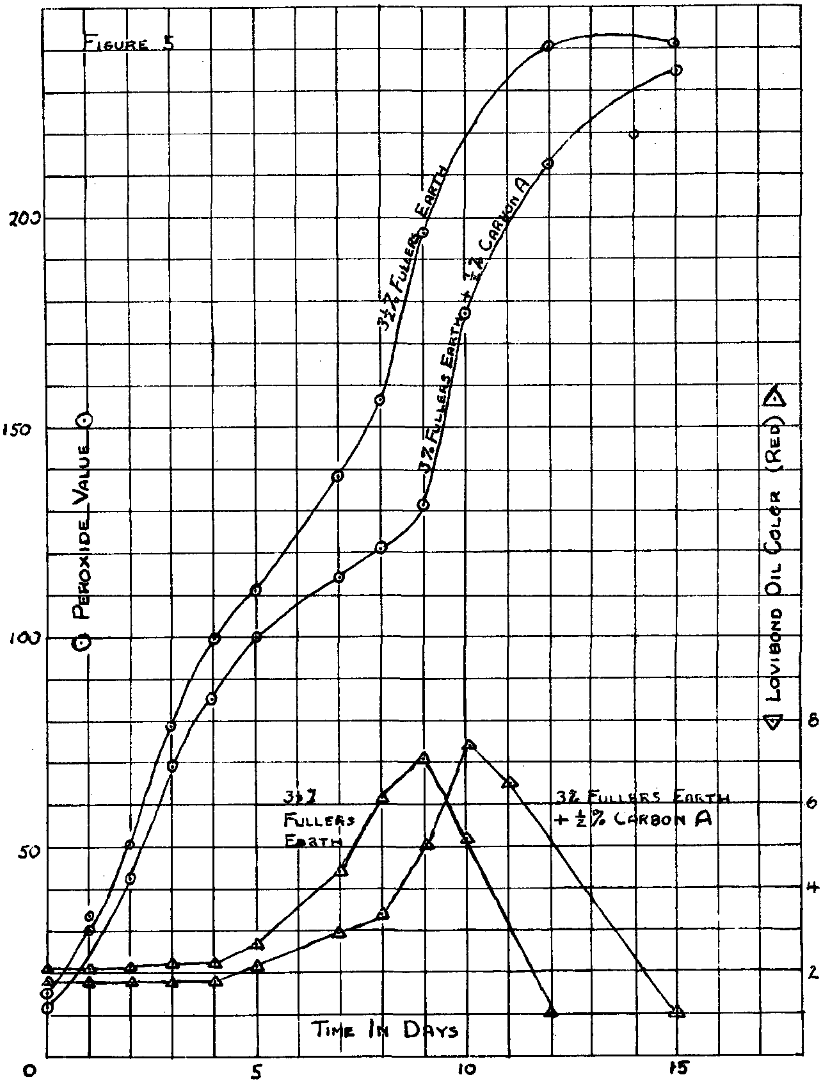

A NEW NON-CRYSTALLIZING GUM ROSIN

By S. PALKIN, Senior Chemist, and W. C. SMITH, Associate Chemist

NAVAL STORES RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPT. OF AGRICULTURE

ROSIN is virtually the only form in which the solid or non-volatile part of pine oleoresin finds its way into commerce. Its vitreous or non-crystalline character is so commonplace as to be taken for granted, and the fact that a substantial proportion of rosin consists of crystallizable acids is almost overlooked. The formation now and then of clusters of crystals within the solid rosin, and for no clearly accountable reason, brings the buyers and sellers of rosin to the realization of this crystallizing tendency and the complications which this slight variation in form entails.

As is well known, the presence of appreciable crystallized material in rosin constitutes a serious objection to its use in various industries, particularly in soap and paper-size-making, where the crystallized rosin, because of its high melting point, enters into reaction with alkali and other materials much more slowly than the uncrystallized, and tends to granulate instead of becoming the smooth, soapy emulsion desired in soap making. Moreover, mere tendency to crystallize, even though crystals have not actually appeared in the original rosin, will bring about crystallization in rosin preparations such as, for example, core oils and adhesives, comprising generally solutions of rosin in linseed oil or petroleum and lubricating oils, thus seriously interfering with their use.

Why some rosins tend to crystallize and others do not, and what testing methods can be applied to rosins to determine the latent or potential crystallizing tendency before any crystallization has taken place are matters now being studied by the Naval Stores Research Division, and a report of this investigation will be published in the near future.

The present paper deals with a rosin fraction, obtainable exclusively from pine gum, which has shown remarkable freedom from tendency to crystallize.

Methods for producing a non-crystallizable rosin constitute subject matter for a number of patents. These may be divided in general into two classes—those involving treatment of rosin by heat, chemical agents, or both[1]; and those involving addition of foreign agents.[2] In either case, it may be pointed out that the net effect comprises addition or formation in the rosin of some foreign agent, that is, a substance not normal to the original rosin, for even heat treatment involves formation of pyrolytic decomposition products of the nature of rosin oils.

The non-crystallizable gum rosin described in this paper is prepared from the liquid portion only of pine gum. This is derived directly from pine gum without the addition (or formation during processing) of any foreign agent, that is, any compound not natural to original pine gum or to rosin. The simplicity with which this non-crystallizing gum rosin can be prepared and the excellence of the product for the purpose intended, should make its preparation attractive to all gum rosin producers and offer to users a greater assurance of rosin of desired quality.

Before proceeding with the few details involved in the preparation of this rosin, it will be well perhaps, to point out some of the elements involved in the character and composition of this rosin and the basic reasons why a rosin prepared from the liquid fraction of gum possesses a high degree of freedom from tendency to crystallize.

It has been known for many years that the primary acids, that is, those existing originally in the pine gum, constituting generally about 75 per cent of the pine oleorosin, consist in part of an easily crystallizable type known as pimaric acids.[3] Of these, two compounds have been identified, α- and β-pimaric acids. More recently, the presence of another easily crystallizable acid, "proabietic acid," has been established by Kurt Kraft.[4] The bulk of acids present, however, comprise a class designated as the sapinic acids,[5] about which, generally speaking, very little is known[6] other than that, as a class, they are unstable, being easily convertible by heat and other means to a series of isomerized acids, including the so-called abietic acid. In addition to the acids, there is also contained, in the non-volatile part of pine gum, some ill-defined non-crystalline neutral bodies known collectively as "resenes."

Now, what happens when gum is subjected to commercial stilling, besides the removal of turpentine? The heat to which gum is subjected in the process causes most of the original acids to undergo a change known to the chemist as isomerization. The degree of isomerization will depend (to some extent) on the length of time and the temperature to which the gum is subjected in the distillation. Since the content of "resenes" is small, gum rosin may be considered to be largely an acid complex consisting, for the minor part, of the so-called "abietic" acids (sometimes called sylvic acids) and of original unchanged gum acids of the more stable type, such as pimaric. These types are both easily crystallizable. The bulk of the rosin, however, consists of a relatively complex mixture of acids in various stages of isomerization, which do not crystallize readily, but may be further changed or isomerized if desired by a higher or more prolonged heat treatment than that normally taking place in the commercial still, or by treatment with a mineral acid, such as hydrochloric acid. By such additional treatment the acids will have been largely converted to abietic- or, even further still, to "pyroabietic-" acids, both of which crystallize readily.

However, this more comprehensive isomerization may be regarded as an artificial process, and not one with which we are much concerned in ordinary gum stilling, except that it must be borne in mind that somewhat higher or more prolonged heating may be the practice of some stillers, and perhaps underheating, in the case of others. These factors will enter into the crystallizability of the resulting rosins to some extent. Also, as will be pointed out in connection with some of the patented processes, heating rosin at temperatures sufficiently high to bring about "cracking" of some of the acids and production of rosin oil-like products, will result in reducing crystallizing tendency of the rosin.

Coming back now to gum, as is well known, there settles out from pine gum or oleoresin on standing, a semi-solid mass of quasi-crystalline nature. Virtually no study has been made prior to the work in this laboratory[7] to ascertain the relative composition of the liquid and settled portions of pine gum. In fact, it has been the general belief that the composition (except as to turpentine content) of this semi-solid mass does not differ materially from that of the liquid portion. Thus an important factor has been overlooked—that in the formation of the semi-solid mass, a very considerable fractionation of the oleoresin naturally occurs in which the viscous liquid portion not only contains a larger proportion of turpentine (a fact generally recognized) than the settled semi-solid portion, but differs markedly from it as regards two very important items. These are (1) content of so-called resenes; and (2) the relative proportions of the two classes of acids, the easily crystallizable acids (pimaric) on the one hand, and the non-crystalline (sapinic, etc.) acids, on the other hand. In this separation, the resenes and amorphous type acids predominate in the liquid portion. Another thing that has not been fully appreciated is that the isomerized acid complexes obtained from these two portions of the gum, respectively, also differ markedly in character and properties, particularly as regards tendency to crystallize, both with reference to the gum products themselves (liquid and semi-solid), and to the rosins from these. Two factors have, in general, been found to exert a vital influence on tendency to crystallize. For the gum itself, these factors are (1) the content of resenes; and (2) the relative content of pimaric acids as compared with that of the sapinic acids. For the rosins obtained from the liquid and settled semi-solid parts as already indicated, a third factor automatically follows, due to the difference in the acid complex resulting from the pimaric and sapinic acids. Since the isomerized acid complexes of the rosins to which these two classes of acids are converted also differ markedly as regards their tendency to crystallize, the net result is that the rosin produced from the liquid portion of gum is characterized by a high content of resenes and isomerized acid complex of the amorphous type acids, and comparative freedom from crystallizable type acids. The

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[1] U. S. Patents as follows: R. C. Palmer, 1,787,281; D. C. Butts, 1,791,658; W. B. Logan, 1,643,276; Avery A. Morton, 2,017,-866; P. Schnorf, 2,074,192.

[2] U. S. Patents as follows: J. N. Borglin, 2,042,877; J. N. Borglin, 2,081,899.

[3] a. Kohler, J. Prakt Chem., **85,** 534 (1912). b. Dupont et Desalbres, Bul. Inst. Pin, **22,** 352 (1936). c. Ruzicka, Balas and Villim, Helv. **7,** 458 (1924). d. Palkin and Harris, Jour. Amer. Chem. Soc., **55,** 3677 (1933). e. Bogert and Hasselstrom, Jour. Amer. Chem. Soc., **57,** 2118 (1935).

[4] Kraft, Ann. **520,** 133 (1935); **524,** 1 (1936).

[5] Dupont and Dubourg, Bul. Inst. Pin, **31,** 581 (1926).

[6] Palkin, Jour. Chem. Ed., **12,** 35 (1935), p. 35.

[7] Palkin and Clark, Ind. Eng. Chem., **26,** 720 (1934).

crystallizing tendency of the rosins made from the liquid portion has thus been reduced to a negligible factor, as shown by the following series of tests.

Methods of Testing for Crystallizing Tendency

Two methods for testing the tendency of a rosin to crystallize have been proposed.[8] One of these methods consists in maintaining a portion of the rosin under test at a temperature of 100-105° C. and noting length of time required for crystals to develop in the mass. Rosins showing an unusually great tendency to crystallize will, under these conditions, develop crystals in anywhere from a few hours to a day. Other rosins which show this tendency to a less marked degree will usually develop crystals within a week. The other proposed method consists in dissolving a portion of the rosin, with the aid of heat, in an equal weight of a vegetable oil such as linseed or a heavy mineral oil such as spindle, bottling and allowing to stand. The length of time required for crystals to develop is a measure of the tendency of the rosin to crystallize. Rosins showing a great tendency to crystallize will show crystals within a day and others which tend to crystallize will develop crystals usually within a month.

The new form of rosin, on subjection to both of these tests, has developed no crystals within a period of three months.

All rosins which show a tendency to crystallize by the above two tests show the presence of the so-called "abietic acid" by the quarter salt method.[9] None of the new rosins showed the presence of the so-called abietic acid by this test.

We have developed a more severe and much accelerated test to determine the crystallizing tendency of rosin. A test tube is filled with broken lumps of the rosin under test and then sufficient acetone to cover the lumps is added. The test tube is stoppered and allowed to stand undisturbed. Rosins showing a great tendency to crystallize by the other methods will show crystals within an hour, and others which tend to crystallize, within a day. The quantity of crystals developed is also a measure of the tendency to crystallize. A large number of samples of gum rosin subjected to this test developed crystals varying from 10 to 75 per cent by volume of the original rosin.

Of fourteen samples of our improved rosins subjected to this severe test, eight showed no crystals, while the remainder showed but few crystals. In no case did crystals develop in a quantity comparable to that developed by normal rosins.

Method of Preparation of the Non-Crystalline Rosin

The matter of separating the semi-crystalline settled portion of pine gum from the viscous liquid portion involves simple decantation or partial filtration. While the general problem of filtering gum as a whole is not a simple one, this problem is now being studied by the Naval Stores Research Division, and a report will appear in the near future. The restricted nature of the partial filtration necessary for the present purpose makes it relatively simple and productive of a very clean gum filtrate which, in turn, yields a bright and clean rosin.

The gum is allowed to stand until substantial settling of the quasi-crystalline mass has taken place. The length of time will depend a good deal on the character of the gum may be allowed to filter (drip) through light weight muslin type bags similar to sugar bags, or, time allowed for crystallization and settling, the greater, generally speaking, will be the freedom of the filtrate from crystallizable acids. The gum may be allowed to filter (drip) through light weight muslin type bags similar to sugar bags, or, preferably, through filter cloth (light weight) spread over aluminum wire screen (about 4 to 6 mesh), suitably supported in a frame. The whole should be enclosed to avoid undue exposure and loss of turpentine. The filtration is allowed to proceed by gravity for from 24 to 48 hours, and under no circumstances should a mechanical or filter press be used, as this high pressure causes liquefaction of the semi-solid crystalline mass and admixture of the latter with the liquid, thus defeating the very object of the filtration.

The filtrate obtained by the cloth filtration is not only free from chips and bark, but remarkably free from fine suspended particles, the quasi-crystalline mass itself evidently acting as a filtration medium.

The following data (Table I), obtained on both laboratory and semi-plant scale tests, are illustrative of the yields of filtrate over given periods of time and under definite conditions of temperature for several samples of gum used.

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[8] E. V. Romaine, Proc. Amer. Soc. Test. Mats., 34, 546 (1934).

[9] a. Dupont, Desalbres and Bernette, Bul. Inst. Pin, 22, 349 (1926). b. Palkin and Harris, Jour. Amer. Chem. Soc., 56, 1935 (1934).

TABLE 1. YIELD OF PARTIAL FILTRATE FROM PINE GUM

Sample*	Wt. of Orig. Gum	Time of Filtration	Weight Total Filtr.	% Total Filtrate	° C. Temp.
1. Longleaf	18 lbs. 4 oz.	17 hrs.	5 lbs.	27.4	30-33°
		25 hrs.	5 lbs. 9 oz.	30.5	
		65 hrs.	6 lbs. 8 oz.	35.6	
		110 hrs.	7 lbs. 1 oz.	38.7	
2. Longleaf and slash	2 lbs. 2 oz.	16 hrs.	12 oz.	35.3	30-33°
3. Mixed gum, stood for 2 years	4 lbs. 6 oz.	110 hrs.	1 lb.	22.9	30-33°
4. Relatively fresh	3 lbs. 12 oz.	24 hrs.	1 lb.	26.7	30-33°
		96 hrs.	1 lb. 6 oz.	36.7	
5. Mixed longleaf and slash—largely slash	35 lbs. 10 oz.	48 hrs.	12 lbs. 12 oz.	35.8	25°
6. Station Exper. Nos. 5, 6, 7, 8	1,700 lbs.	48 and 120 hrs.†	387 lbs.	About 22.8	23-28°

*Samples 1-5, inclusive, were placed in muslin (sugar) sacks which were then suspended, and the filtrate on dripping was caught in glass or porcelain receptacles.

The larger samples were filtered at the Naval Stores Station in a manner similar to that in which rosin is strained, using a one-piece strainer and vat made of aluminum. Muslin, however, was used over the strainer wire rather than batting.

†Three barrels of gum were allowed to filter for 48 hours, and one for 120 hours.