

cance of these changes. That tree which shows the most marked variation, A2, is a healthy, vigorous tree, from which variations would be least expected. Nor can an explanation be offered for the wide variations in the optical rotation of oils from the same species. All of the trees in Series A are located within 20 yards of each other and have, therefore, the same general conditions of climate, light and soil. Fractionation of the volatile oils from these show practically the same rise in boiling-point for the same volume of distillate. It would seem, therefore, that these volatile oils, consisting so largely of pinene, are mixtures principally of dextro- and levo-pinene, the preponderance of the one or the other determining the optical rotation.

UNIVERSITY OF NORTH CAROLINA
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A METHOD OF ANALYZING SHELLAC.¹

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The method of analysis which is in most common use at the present time, both in England and in the U. S., for the determination of the amount of rosin in shellac, is an indirect method depending upon the different powers of a shellac and of rosin to absorb iodine from a suitable solution. Different operators prefer different methods of making this test, some preferring to use the old Hubl method, and others the more modern Wijs method, as modified by Langmuir. Either of these methods is capable of giving reasonably satisfactory results, although the Langmuir method is certainly much to be preferred, both on the score of accuracy and of speed. Another method which is in use is that proposed by Parry, depending upon the solubility of the resinate of silver made from common rosin, in ether, while the corresponding resinates from shellac are insoluble. This method labors under several disadvantages and sources of error, of which the two principal ones are the solubility of the unsaponified portion of the shellac in ether, and the danger of a decomposition of the resinate of silver before it can be separated and determined.

A direct method of separating shellac and rosin and recovering the rosin, at least, in a substantially unchanged form, is greatly to be desired and several experimenters have attempted to make such a separation by taking advantage of the solubility of rosin in petroleum ether, a solvent in which shellac is insoluble. No method of extracting from even a finely pulverized sample of shellac the portion soluble in petroleum ether seems to be capable of removing more than a small part of the rosin contained in the sample.

¹ Read before the New York Section on March 6, 1908.

Shellac dissolves in alcohol, except for the wax contained in it; petroleum ether dissolves to some extent in alcohol and it was thought that by first dissolving the shellac to be analyzed in alcohol, then adding to the solution all the petroleum ether which it would dissolve, and then adding water, so as to so dilute the alcohol that it would no longer have any material solvent power upon either rosin or shellac, there should result a separation of the dissolved petrolic ether containing in solution the rosin and the wax, but free from the resinous constituents of the shellac. Upon trying this process, it appeared that it was correct in principle, but that on account of the limited solubility of petroleum ether in alcohol, the separation was not quite complete. Upon substituting for ordinary alcohol, glacial acetic acid, or absolute alcohol, in which the sample of shellac to be examined is dissolved and then adding to it petroleum ether, which is miscible in all proportions with acetic acid, or absolute alcohol, it was found practicable to combine with the rosin and the wax so large an amount of petroleum ether, that upon adding water, an almost complete separation of the rosin and wax from the resinous part of the shellac could be effected.

Based upon these facts, the following process was devised: Dissolve in 20 cc. of glacial acetic acid (about 99 per cent.), or the same volume of absolute alcohol, 2 grams of the sample to be analyzed. This requires a gentle heat. Add to the solution, after cooling, 100 to 300 cc. of petroleum ether, boiling under 80°. This addition of petroleum ether should be made slowly, because the addition of so large an amount of petroleum ether precipitates from its solution a part of the shellac, combined, apparently, in case acetic acid was the original solvent, with acetic acid to form a liquid precipitate. It is manifestly desirable that this precipitation of part of the shellac should not be effected by too sudden an addition of petroleum ether, as it might then contain some rosin carried down mechanically with it.

We now have a solution containing both petroleum ether and glacial acetic acid, or absolute alcohol, and containing in it, in solution, all the rosin, all the wax and most of the resinous part of the shellac. Add now to this solution, drop by drop, 100 cc. of water, agitating the liquid during the addition. The water "unites with" the alcohol or acetic acid, and separates from the liquid the petroleum ether with whatever is soluble in petrolic ether. This includes the rosin and the wax. The shellac is also precipitated, but as it is insoluble in petroleum ether it remains as a precipitate suspended in the diluted alcohol or acetic acid. The separation of the two liquids takes place very rapidly, and it is an easy matter to effect a complete separation of the two layers in a separating funnel. The petroleum ether layer is washed once or twice with water and then filtered through a dry paper into a weighed flask, from which the petroleum

ether is then distilled off, leaving the residue of rosin mixed with wax, which is weighed. To the weighed residue neutral alcohol is added, and the flask heated to dissolve the rosin in the alcohol. The liquid is then titrated with N/5 or N/10 caustic potash. This gives a measure of the amount of rosin present, as the average combining equivalent of rosin does not vary greatly from 346. This is the figure used for this titration in the Twitchell process. It is much better, however, not to depend upon his determination of the rosin but to proceed to an actual separation by adding to the neutralized alcoholic solution, a distinct excess of alkali, and a sufficient quantity of petroleum ether; the mixture is then transferred to a separating funnel, thoroughly agitated, and some water added. The liquids are then separated, the petroleum ether layer being washed with water, and the alcoholic solution of the rosin extracted once more with petroleum ether. The petroleum ether solutions are then united, the petroleum ether distilled off, and the residue of wax weighed. The alcoholic solution containing the rosin is then boiled until the alcohol has been expelled, and, if necessary, a further addition of water made; then dilute hydrochloric acid is added, so as to precipitate the rosin. This should be done in a weighed flask; the acidified liquid can now be decanted off through a wet filter paper so as to leave behind in the flask the major part of the rosin, which is washed with water. The remainder of the rosin upon the filter paper after sufficient washing, is extracted with petroleum ether back into the weighed flask from which the water has been decanted as perfectly as possible. Upon distilling off the petroleum ether, the rosin is left behind in a condition to weigh. If the whole of the last traces of water have not been removed by the distillation with petroleum ether, it is well to add a further quantity of dry petroleum ether and distil again.

Attempts were made to use other solvents, particularly coal tar benzene instead of petroleum ether. It was found, however, that benzene dissolved considerably more out of the shellac than the wax.

If it is desired to determine only the rosin in the shellac, it is unnecessary to distil off all the petroleum ether from the solution containing the wax and the rosin. This solution may, instead, be treated directly with an alkali capable of combining with the rosin, while leaving the wax unattached. The most convenient method which I have found for accomplishing this is to add to the petroleum ether solution, after filtering it to remove from it anything which it may contain in suspension, a solution of sodium hydroxide in absolute alcohol. Such a solution I have found it convenient to make by dissolving in ordinary 95 per cent. alcohol the appropriate amount of metallic sodium. Such a solution, when added to the petroleum ether solution, mixes perfectly with it, and the alkali combines with the rosin, and the mixed solution allows the saponified

rosin to be extracted from it by agitation with water, or better, with slightly diluted alcohol. Instead of using a solution of sodium hydroxide in absolute alcohol, it should be possible to use the method of separating rosin from neutral substances in petroleum ether solution, that is used in the Twitchell process of determining rosin in admixture with fatty acid. This consists in agitating the petroleum ether solution with an alkaline aqueous solution, containing some alcohol, made by dissolving one gram of potassium hydroxide with 10 cc. of alcohol in water, and diluting to 100 cc. I have found the other method of procedure advantageous, however, and believe it to give a more exact separation. The solution drawn off from the petroleum ether, after extraction by alkali and containing in solution the rosin, combined with potassium or sodium, together with whatever alcohol has been used to promote the combination and to facilitate the mechanical separation of the two liquids, is heated for some time to remove the alcohol, and is then acidified with hydrochloric or with sulphuric acid to precipitate the rosin. The precipitated rosin is then weighed as before.

Without entering into a discussion of the exact chemical composition of shellac wax, it may be proper to state that the wax may be separated commercially from shellac by two essentially different methods, which will probably give waxes having somewhat different compositions. If the shellac is dissolved in an alkaline solution and the wax which remains in suspension is filtered out, it is probable that different results will be obtained from what would be obtained by the other process, consisting of a solution of the shellac in alcohol, and filtration of the solution to remove the wax which will then remain in suspension. It is to be expected that these two processes of solution would leave, in the undissolved wax, small amounts of ingredients of different characters, and, furthermore, the alcohol used in the second process would dissolve small amounts of the wax which would probably be quite insoluble in an alkaline aqueous solution. Again, it is quite probable that a caustic solution would behave towards shellac wax somewhat differently from a dilute carbonate solution. For the sake of uniformity and simplicity, I am assuming that shellac wax is quite free, when pure, from all acid substances capable of uniting with free alkali. It is, nevertheless, true that the user of shellac who wishes to have a determination made of the amount of wax which it contains, usually desires this information in order that he may know how much of the shellac will remain undissolved in alcohol. This amount of insoluble wax will, of course, vary to some extent, depending upon the strength of the varnish that he prepares with it, that is to say, the number of pounds of shellac which he uses to a gallon of alcohol. As the analyst can hardly be expected to take account of this in making his test, it appears more rational to regard as

wax the whole of those matters contained in the shellac that remain insoluble in an alkaline solution.

In making a determination of the amount of wax in a sample of shellac, by this method, it is to be observed that some constituent of shellac wax is evidently only difficultly soluble in petroleum ether. Upon submitting several portions of the same lot of shellac to analysis in this way, the only difference made in the different determinations being that varying amounts of petroleum ether were used, the series of analyses gave, with increasing amounts of petroleum ether, increasing percentages of wax, until the proportion of about 125 to 150 cc. of the solvent to 1 gram of a shellac containing about 5 per cent. of wax was reached. It may be that by using some other solvent such as benzene for the determination of wax in this way, a smaller amount will suffice, but as it seldom happens that only wax without rosin is to be determined, petroleum ether is the most generally applicable solvent. The solubility of rosin in petroleum ether is so easy and complete that no difficulty is experienced in extracting from 2 grams of shellac 50 per cent. of rosin, using 100 cc. of petroleum ether.

Whenever in the course of an analysis by this method a quantity of material is separated by acidifying the aqueous solution which should contain the rosin, its identity may be established with some certainty by determining its iodine figure by the Langmuir method, and its acidity by titrating with alkali in alcoholic solution.

The petroleum ether referred to here is a solvent made by redistilling 71° Bé. benzine, separating for use that part which distils below 80°. This fraction constitutes a large proportion of 71° benzine, and such a redistillation gives, at a comparatively small cost, a satisfactory solvent for the purpose. If a determination of only the rosin is desired, it is of course unnecessary to be very particular as to the volatility of the solvent used, as it is unnecessary in such case to distil it off before extracting the rosin by alkali.

By treating pure shellac according to this process, it is possible to separate from it a small amount, sometimes as much as 1 per cent., of materials soluble in petroleum ether. This small amount of resinous matter, when examined, proves to be something essentially different from common rosin. Its odor and its low iodine figure indicate that it is some resinous constituent of shellac, perhaps a small amount of the major constituent, which is slightly soluble in petroleum ether. As it is difficult to imagine that by this process rosin if a normal constituent of pure shellac would escape detection, and as the small amount of resinous matter here obtained is essentially different from rosin, it is reasonable to conclude that, contrary to the idea held by many, common rosin or a material similar to it, is not a natural constituent of pure shellac, but

that any rosin or colophony, which can be separated in a state of reasonable purity from the sample of shellac, was originally added to the shellac, as an adulterant.

The process here described allows the analyst to separate in a form convenient for exhibition either as evidence in court or as an ocular demonstration for his client, any rosin which may have been added as an adulterant to shellac.

Shellac varnishes may contain beside true shellac not only rosin, but other gums and resins soluble in alcohol. It becomes, therefore, a matter of interest to ascertain how some of these other resins behave when treated by this process. Two samples of manilla, when treated, using absolute alcohol as the first solvent, gave respectively, 41.2 and 43.3 per cent. of matter soluble in petroleum ether. The acidity of these two lots of matter soluble in petroleum ether was in the case of the first sample such that 1 cc. of normal alkali neutralized 411.7 milligrams and in the case of the second 470.7 milligrams. Two samples of Kauri gave, respectively, 37.9 and 27.0 per cent. Upon titrating with standard alkali these portions soluble in petroleum ether, it appeared that 1 cc. of normal alkali was capable of neutralizing 903.6 mg. and 742.5 mg., respectively. Of Sandarac, two samples, when similarly analyzed, gave 34.96 and 36.19 per cent., having such an acidity that of the first 541.2 mg. would neutralize 1 cc. normal alkali, and of the second, 552.5 mg. would neutralize 1 cc. Of Dammar, 89.9 per cent. proved to be soluble, while the resin of *Shorca roburta*, a sample of which was kindly sent by Mr. W. Risdon Criper, of Calcutta, gave 69.5 per cent. of soluble matter.

A number of attempts were made to effect a satisfactory separation of the wax before separating the rosin from the shellac. It was found, however, that on account of the solubility of wax in alcohol and in glacial acetic acid, this separation could not well be made by filtering out the wax before the addition of petroleum ether. Neither were attempts which were made to separate the wax by a preliminary solution of the shellac in aqueous alkali successful in furnishing a method that at all approached in feasibility to the method already described.

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THE VOLATILE OIL OF *PINUS SEROTINA*.

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Scattered among the forests of Long Leaf pine along the Atlantic seaboard, there are found, usually in mixed stands, patches of Pond pine (*Pinus serotina*) and Loblolly pine (*Pinus taeda*). These pines are seldom subjected to turpentine, as the yield of oleoresin is not so plenti-