# STUDIES UPON RESINS.

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Resins have, at different times, been subjected to chemical treatment and as far as some of them are concerned, we have quite valuable knowledge of the same. We know of abietinic acid in rosin, we know of a peculiar facility of reaction between some of them with phenol, but still, if asked, what is a resin, chemically speaking, cannot give an explanation.

## I.—COPAL RESIN.

I have begun to study, qualitatively, a resin of great practical importance in the manufacture of varnishes, the so called copal. The difficulty which meets us at the outset of such researches is this : Are we always sure of finding the same raw material under such a name, for example, as copal? What is copal, not chemically but commercially?

We find soft copals, such as damar, which is soluble in ether, but there are other half hard, and still other perfectly hard copals which only partially dissolve in different solvents, but which can be made soluble by allowing them to suffer previously a chemical change. After this, however, we have no longer to do with the raw product "copal," but with a product of decomposition of the same. The soft copals are said to be found mainly on the islands of Sumatra, Java, Molucca and the Philippines, also in Australia. The hard copals are imported via Calcutta and Bombay from some places in Africa. All of these have very different appearance and different physical properties, so different that it seems almost impossible to attribute the same name to them. Their origin is not very clear. The hard copal is called hard animi in England ; it is imported into Europe via Calcutta and brought there by African traders from Zanzibar and the adjoining coasts. The hard copal from Bombay is brought to that place from Madagascar. It is found in Madagascar, Mauritius, Bourbon and is said to be furnished by a tree *Hymenæa Verrucosa.* (Jussien calls it *Taurouyon*). On l'Ile de France the tree is called *copallier.* We learn also that *Hymenæa Courbaril* of Cayenne furnishes a substance similar to hard copal. (Henry Violette, Fabrication des Vernis, p. 302 to 304).

Now, the fact of a vegetable origin of copal seems to be evident. But the growers mix pell mell, soft and hard copals, with other resins and ship them as hard copal. The dealers assort these mixtures and the manufacturers of varnish must rely upon them as well as upon their own knowledge in buying a uniform article. So much as to the origin of copal. The chemical properties of hard copal, as far as the varnish manufacturers are interested in them, are the following: it is insoluble as a whole in alcohol, ether, and oil of turpentine, but becomes soluble in these latter two when previously heated.

Since most hard copal varnishes are solutions in oil of turpentine and linseed oil, we have to remember how the manufacturers proceed. They heat the copal until it melts and continue this heating according to routine. At the same time oil of turpentine is heated to boiling, and at a certain stage of this manipulation the two hot liquids are mixed together in certain proportions. If the copal is not hot enough, and if the hot oil of turpentine is not allowed to run slowly into the former, a clear solution is not obtained. That a great manufacture (dangerous also, as far as inflammability and irritating exhalations are concerned), rests thus upon a most empirical basis is surely the reason for the issue of innumerable patents in regard to changes in the same, changes which, however, have not generally been adopted. (See Ure's Dictionary, 7th Ed., p. 1055.)

But the chemist may approach this task in a different way. He arrives at the knowledge of the real composition of a compound or a mixture through the study of products of decomposition of the same. The synthesis of indigo was only effected after a most perfect study of its products of decomposition had been made.

We know from the above that copal suffers decomposition by heat in such a manner as to leave a residue soluble in boiling oil of turpentine to a varnish. Consequently the exact conditions of this decomposition should be ascertained. Heating copal slowly in a flask connected with a Liebig's condenser, a light flowing distillate which has an agreeable odor, suggestive of terpenes, even of lemon, passes over at first. This odor indicates the presence of the *limonen*, of *Wallach*. (*Ann. Chem., Liebig*, **252**, *108.*) Shortly after this, vapors arise which cannot be condensed and which are of an irritating nature, the mass turns darker brown, and the boiling continues in this way until almost all of the copal is destroyed. Performing this experiment with the aid of a thermometer in a fraction flask, we see the aromatic oil distil at temperatures above 100° C. up to 170° C. or 185° C. * The mass boils quietly, then the white vapors, which partially condense to a liquid of empyreumatic odor, begin to appear when the temperature of 215° C. is reached, the mass turns very dark, boils quietly without sending off visible vapors and the thermometer *falls* suddenly and rapidly to 170° C., or even below that temperature. It seems to follow from this, that while up to 215° a fractional separation of a mixture is going on, when this temperature is reached the heat applied is partly used for more profound inner decomposition of the residue in the flask. If, therefore, the copal be only heated to 182° C. until no more distillate is obtained, and then allowed to cool, we avoid this latter decomposition.

Copal thus heated to 182° C., when allowed to cool, yields a very brilliant glass-hard, translucent resin, which is soluble with the greatest facility in cold or warm oil of turpentine.

The distillate obtained forms ⅓ of weight of the raw copal used.

In order to obtain the first volatile oil of agreeable odor in purer

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* In all the data given in this paper in regard to temperatures, the thermometer is always supposed to be in the *vapor* above the liquid and never immersed *in* the liquid. In a subsequent paper experiments will be reported which I have made with a view to determine both temperatures simultaneously, those of the melted gum as well as of the vapors formed.

form, distillation in a current of steam was resorted to. The oil obtained floated on water, but was not obtained in quantities sufficiently large.

The experiment was repeated on a larger scale (with the liberal aid of Dr. Alsberg and in his factory) in a copper still and with 45 pounds of steam pressure.*

Then again the cooler was not adequate to allow full condensation, and the room was filled with an agreeable odor suggestive of lemon terpenes. The residue in the still, when cold, was very hard, but porous and consequently brittle. It did not dissolve in oil of turpentine.

Next it was ascertained what liquids would dissolve copal without previous treatment. It is said that the distillate obtained from copal by destructive distillation is a solvent for melted copal. But the evil odor makes this unmanageable. It was proved to be correct, as found by former investigators, that aniline and its homologues dissolved copal very readily.

Nitrobenzol or chloroform dissolved copal, the former better than the latter, which, like almost all commercial chloroform was not free from an inflammable admixture, perhaps undecomposed acetone.

Phenol dissolves copal well. This is a known and patented fact. I found cyneol to be an extremely good solvent for copal. (For Cyneol, see *Ann. Chem. Liebig*, **225**, *295*.)

An astonishing reaction took place when copal was treated with benzaldehyde. This latter dissolves in a most perfect manner at first. Shortly afterwards the whole mass thickens to a light amber colored jelly, not unlike new peach gum, only much softer. It is almost impossible to handle this mass. After some experience it is possible to bring it into a flask and to subject it to distillation. Better results are obtained when ground copal is put into a flask and the $C_6H_5COH$ added. A perfectly clear solution is obtained. At 80° C. the jelly form is reached, and care has to be taken that continued heating does not crack the flask.

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*I also owe to Dr. Alsberg's kindness a liberal supply of a most uniform, rather pale copal (Kauri gum), of a quality superior to that ordinarily used for varnishes.

Then thick yellowish white fumes are driven through the cooler and $C_6H_5COH$ and some $H_2O$ distil off. Later an oil which irritates the eyes follows. Finally an oil distils which condenses to thick white crystals either in the condensing tube or according to temperatures in the receiver. This crystalline mass is soluble in ether and also in benzaldehyde. When this experiment was performed after prolonged treatment of copal with benzaldehyde, under an upright condenser, the result was similar. On distilling, the temperature must not rise above 215° C. or more profound decomposition takes place.

A peculiar fact connected with this experiment was that an increase in weight of 8% was noticed, when the quantity of products obtained was compared with the quantity used. This is suggestive of oxidation through atmospheric oxygen, as far as the distillate is concerned. These experiments will be followed up closely and reported upon later.

Resuming the study of solvents for crude copal, oil of turpentine was inverted at + 270° and seemed to be a solvent. Glacial acetic acid dissolved copal partially. Carbon disulphide is taken up by copal in large quantities, copal being a colloid with the former. On adding more disulphide the plastic mass rises to the surface and on filtering and drying becomes brittle. The solution of $CS_2$ was evaporated on a water bath and furnished a gummy, light yellow colored mass of aromatic odor. The plastic mass when exposed to air resumes a hard and brittle form. Copal heated together with glycerine without pressure does not form a fatty substance. The experiment in pressure tubes has not yet been performed.

When conc. $H_2SO_4$ acts upon copal, sulphur dioxide is generated and the mass turns dark brown.

Chromic acid, even boiling, does *not* act upon copal.

When the oxidizing mixture of potassium dichromate and $H_2SO_4$ is used a strong action takes place and an odor suggestive of that of the dried leaves of *Asperula Odorata* is noticed.

Strong sodium hydrate of 40° Be. does not act appreciably.

Potassium permanganate attacks copal on boiling.

When boiled with nitrosylsulphuric acid, a reaction, which is not violent takes place. It appears that a nitro product is formed. The product of reaction when poured into water separates yellow flocks which dissolve in alkalies with mahogany color.

Sulphur introduced into boiling copal develops hydrogen sulphide. The mass turns very hard and black, and becomes unmanageable. For instance, it is not easily attacked by alkaline solutions.

A very strong reaction takes place when reducing substances are brought together with copal. Alcoholic ammonia acts strongly when warm. The alcoholic solution deposits besides sulphur, a *white* solid compound when neutralized by acids. The residue that did not dissolve in alcohol when boiled with water puffs up to a very porous mass, not unlike beaten white of egg. This mass when dried is easily crushed to a fine powder which is entirely volatile when gently heated.

Watery ammonium sulphide, reacts on boiling, upon copal. The warm solution is blood red but on cooling becomes lighter colored. The residue after boiling with water and treating with dilute $H_2SO_4$, develops lemon odor.

Watery ammonium hydrate was used in order to see whether an abietinic acid salt might be obtained. The product of the reaction turns at once snow white: it does not float upon the liquid but sinks in it as a heavy white powder. Also this ammonium salt volatilizes entirely, without leaving a residue.

Solid potassium cyanide fused with copal developed very bad odors and was abandoned.

The reaction of grape sugar in alkaline solution is an exceedingly lively and sudden one, which could not be tempered.

Also alcoholic potassium reacts with copal when moderate heat is applied.

Strong hydrochloric acid attacks copal slightly.

Zinc dust heated with copal develops currents of hydrocarbons, some of which do not condense, while iron powder is without action. Zn and HCl do not show any reaction.

The experiments performed so far are those of destructive distillation, of oxidation and reduction as stated above. Furthermore, the remarkable reaction with aldehydes, such as benzaldehyde and that with nitrosylsulphuric acid to form nitro products and the formation of an ammonium salt which is as volatile as ammonium chloride.

All these experiments will next be performed quantitatively, and should then allow definite conclusions in regard to my assumption that the crude copal consists of three typical components, a terpene, an easily oxidizable hydrocarbon not a terpene, and an acid which may be homologous with abietinic acid. This acid has the peculiarity of being an amorphous, glass-hard and translucent mass.

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