C - 1

Cross References:

Natural Gums - 1011-A
Resins-General-1011
National P.V. & L. ASS'N.

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[illegible]
[illegible]
[illegible]
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Philadelphia Laboratory
September [illegible], 194[illegible]

MEMORANDUM REPORT # M-[illegible]:

GENERAL [illegible]

As a result of contacts with the National Paint, Varnish, and Lacquer Association, Dr. [illegible] Martin, a government consultant on WPB (formerly Associate Horticulturist at the University of Arizona) who instigated the present work on creosote bush resin, has submitted three pounds of rough powder (DS-16039) and ten pounds of Acetone Extract (DS-16040) of creosote bush resin for our evaluation. These resins are unlike any other materials which we have tested and were suggested by Dr. Gardner's organization as having film forming properties and being worthy of investigation as reported in the Scientific Circulars #617 and #6[illegible]. The supply is practically inexhaustible since the bush is found in abundance in the Southwestern United States and Mexico as wild growth. No cost has as yet been established.

Summary:

Our examination of the two samples indicate that the rough powder, which is thought to be ground creosote bush, cannot be used as a raw material to develop a film forming substance due to its lack of solubility and heat stability, whereas the acetone extract appears to offer possibilities as a film former because of its heat advancing characteristics and its chemical activity with oils and formaldehyde. Although these characteristics are desirable, they are off-set by the dark color of the gum, the presence of dry inhibiting compounds and the necessity of using high solvency solvents. Considering these facts, the resin may find use in black baking insulating enamels, [illegible] enamels, in [illegible] finishes as a heat stabilizer and other places where high color is not a disadvantage, chemical inertness is desired, and a [illegible] finish can be used. These possible uses are contingent on the cost of the material as compared to the resins now used in such products. Probably a better [illegible] could be obtained if it could be refined or treated in such a manner as to [illegible] inhibiting factors, and if the cost [illegible] amount of development work [illegible] resin can be made into a [illegible]

Experimental Details:

1. Rough Powder:

A number of tests were conducted to determine the nature of the rough powder, which is brown in color with no hardness to the touch. It was now completely soluble in any type solvent and only slightly soluble in ketones, esters, alcohols, and nitroparaffins. It was practically insoluble in aliphatic and aromatic hydrocarbons. It decomposed without melting when heated. A stock solution was obtained from the rough powder by acetone extraction with the majority of the powder remaining after extraction. On evaporation of the solution it produced a heavy bodied liquid which appeared similar to the acetone extract furnished us. The characteristics of both extracts were also similar. Attempts to produce a varnish with this powder were unsuccessful, the powder remaining undissolved in the oil after heating to 560°F. Boiling the oil and powder at this temperature resulted in an infusible black mass. As the only use that we could make of the powder was to produce an acetone extract, no further work was carried out with this sample.

2. Acetone Extract:

In the evaluation of the acetone extract from the supplier, high spot tests were made to characterize the resin. The extract is a black liquid having a very heavy body and a gallon weight of 10.25 pounds/gallon. The melting point of the solid resin is 93°C by the ring and ball method. It has a distinct aromatic odor resembling gum benzoin.

The acetone extract is miscible with ketones, esters, ethers, and alcohols. Nitroparaffins had slightly less solvent action on the resin than the solvents mentioned above. The extract is insoluble in both aliphatic and aromatic hydrocarbons. Addition of small amounts of mineral spirits kicked out the resin from an isopropyl alcohol/acetone solution.

In evaluating the resin for film forming properties, a solution in isopropyl alcohol and acetone produced a gritty film which was still slightly tacky after six days dry. In order to determine the effect of driers on the resin, a solution of the resin in cyclohexanone was made containing the following percentages of driers - cobalt 0.05%, manganese 0.05%, and lead 0.2% - which were added in the form of naphthenates dissolved in cyclohexanone. The film from this solution was slightly tacky for five days and was tack free after eight days. The film also showed bad seeding, probably due to granular impurities in the resin. The film was hard and brittle with good adhesion to glass. When the film was baked at 200°F. for [illegible]

hard and brittle with fair adhesion, but [illegible] as evidenced by cycloling.

As the resin has phenolic groups present, it is possible with formaldehyde. Addition of paraformaldehyde at this stage produced a very thick resin product at 400°F. which [illegible] did not thin out but charred. This resin is soluble in xylol or cyclohexanone. As heat reactive phenolic resins are known stabilizers for vinyl polymers both the acetone extract and the paraformaldehyde treated gum were evaluated as thermal stabilizers. Ten percent of the resin on the solids of the vinyl solutions gave only slight stabilizing action while five or ten percent of a paraformaldehyde treated resin gave a definite stabilizing effect.

3. Varnishes:

In order to make a varnish, the acetone extract was first evaporated to produce a 100% solid resin. A twenty-five gallon oil length varnish was made using Pittsburgh Selected #200 Oil. It became clear on glass after heating to 580°F. There was considerable foaming during the hold at 580°F. indicating a reaction between the resin and the oil, which was indicated also by the rapid bodying of the varnish. The finished varnish was soluble in mineral spirits, petroleum xylol, and cyclohexanone, but not in isopropyl alcohol. The best solvent was petroleum xylol. After eight days the film was still very slightly tacky. A bake at 300°F. for 1/2 hour was not sufficient to make the varnish tack-free, but increasing the bake to 350°F. for 1/2 hour produced a tack-free film with fair hardness and adhesion to steel and good flexibility.

The presence of phenolic groups tend to inhibit the dry, so attempts were made to produce air dry varnishes by treating the varnish with paraformaldehyde. Another twenty-five gallon varnish was made using alkali refined linseed oil. The oil and resin in the proportion of a 12-1/2 gallon oil length varnish were heated to 580°F. where the varnish became clear on glass. On cooling to 350°F. paraformaldehyde was added and after the addition was complete, the mixture was heated to 400°F., at which point the varnish gelled. However, the addition of the remainder of the oil and heating to 580°F. redispersed the gelled material. Body "Y+" was obtained at 52% solids with petroleum xylol after a total elapsed cooking time of one hour and 14 minutes. It was also soluble in mineral spirits but gave a considerably heavier body with it than with petroleum xylol.

The addition of driers produced a reaction as the varnish bodied very rapidly. Though this varnish had somewhat better dry, it was still slightly tacky after 7 days. When baked on steel for 1/2 hour at 300°F. it was tack-free with approximately the same hardness and flexibility but less adhesion than the varnish without the paraformaldehyde treatment which required a bake

of 1/2 @ 350°F. to dry tack-free.

Baked films of these two varnishes were tested for chemical resistance in comparison with a butyl phenol resin varnish. Spot tests showed that the creosote bush resin varnishes failed after 2-1/2 hours contact with 5% caustic soda while the phenolic varnish was unaffected. The experimental varnishes failed after 5 hours contact with 25% sulfuric acid, the control was again unaffected. The varnishes were satisfactory after 20 hours immersion in V.M & P. Naphtha with the control somewhat softer than the experimental. In water resistance the control was somewhat softer than the bush resin varnishes. The varnish was satisfactory in oil resistance. Although the creosote bush resin varnish failed in 2-1/2 hours in contact with caustics, this is a better performance than that with phenolic modified rosin varnishes.

The two varnishes have definite staining through characteristics when coated with a white baking enamel, the varnish with paraformaldehyde having slightly less staining than the one without paraformaldehyde. Hence, we feel that creosote bush resin varnish would be unsuitable as a primer vehicle for white industrial enamels, where its chemical resistance might be of interest.

Further details of this work may be found in the writer's notebooks #2871, pages 172-173 and #2893, pages 87-115.

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