SOME STUDIES OF RESIN FORMATION FROM CASHEW NUT SHELL OIL

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by

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The writer also wishes to thank General Foods, Inc., for furnishing the cashew nut shell oil, and for the method used in the separating and decarboxylating of anacardic acid found in sections V-B - 1 and 3, and V-B - 4 respectively.

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I. INTRODUCTION

Since the discovery of Bakelite a great deal of research has been done on the polymerization of synthetic and naturally occurring substituted phenols with formaldehyde to obtain modified phenol-formaldehyde resins. Coming under the latter category is the oil of the cashew shell, formerly a waste by product, which is made up essentially of cardanol (see page 10) and anacardic acid (see page 10). This paper will deal with further studies of cashew nut shell oil and formaldehyde especially in the presence of certain modifiers.

II. HISTORICAL

The cashew nut made its first appearance in the literature in 1911 when Schenk (1) reported it as a new confection. From then until 1922 the kernel of the nut was studied and the husk was given no attention at all. In 1923 however J.J. Sudborough (2) found that the husk contained 39.8% oil with d_{26}1.0131, acid value 107, saponification equivalent 119, iodine number 296 $n\frac{41.5}{d}$ 1.5158, and was made up essentially of anacardic acid ($C_{22}H_{32}O_3$) and cardol ($C_{32}H_{52}O_4$), both being substituted phenols with unsaturated side chains.

These facts point to resins of both "A" and "C" type, but the problem remained untouched until 1927 when Harvey (3) obtained a patent for the treatment of the oil with nitric acid, etc., or formaldehyde which yielded a product suitable for molding or lacquers. From then on much work has been done on the problem with M.T. Harvey doing the major portion. In the same year he (4) patented the polymerization of cashew nut shell oil and glycerol induced by heat and catalyst. In 1928 another patent was issued to Harvey (5) covering the drying of cashew nut shell oil with a metal such as Cu, Al, or Pb. In 1928 he (6) also received a patent for the treatment of cashew nut shell oil with ammonia, ammonium hydroxide, etc. to produce compounds that varied in color from red to violet useful as coloring agents. A product useful for paints and varnishes was made by heating the oil with nitric acid and patented by Harvey (7) in 1929. In the same year he (8) patented an insulator made from cashew nut shell oil and formaldehyde with hydrochloric acid as the catalyst.

A process for extracting the oil from the shell was devised and patented by Hughes (9) in 1931. The nuts are subjected to a sudden change in temperature from normal to charring, bursting the cellular structure of the shell and allowing the liquid to run out. A compound suitable for insulation was prepared in 1931 by Harvey (10) by vulcanizing cashew nut shell oil with rubber. Also in 1931 Harvey (11) patented a product prepared from cashew nut shell oil and formaldehyde.

A.J. Haagen Smit (12) in 1931 proved the structure of anacardic acid to be 2-OH, 1-COOH 3-n$C_{15}H_{27}$ benzene.

Harvey again in 1932 patented a great deal of work including, (13) cashew nut shell oil used as a plasticizer with cellulose esters such as cellulose acetate, (14) an insulator from cashew nut shell oil and a drier such as manganese, (15) a water-proofing material from the oil for waterproofing of concrete surfaces, etc., (16) a red to violet coloring material from the oil and ammonia and formaldehyde, (17) a resin obtained by treating cashew nut shell oil with an acid and oxidizing with nitric acid, (18) a varnish containing a modifier of

China wood oil, (19) a varnish for inside of iron food containers.

Ryan in 1932 also patented a varnish (20) made from cashew nut shell oil, a congealed vegetable oxidation product such as copal gum, and a suitable catalyst.

In 1933 Harvey (21) prepared a compound consisting of the oil, stearin pitch and hexamethalene tetramine.

In 1934 a product from cashew nut shell oil and casein with an alkaline catalyst was prepared by Harvey (22).

The first mention of distillation was noted in 1934 when Harvey (23) reported and patented a method for the distillation of cashew nut shell oil at a temperature of 300° to 400° C. at atmospheric pressure which yielded a product of germicidal phenolic character.

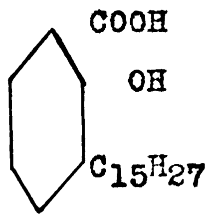
Damitz (24) in 1935 reported a brittle fusible resin from cashew nut shell oil and ester gum heated together at a temperature of 315° C.

Dickey (25) also in 1935 polymerized cashew nut shell oil with rubber to give a material suitable for typewriter platens, etc.

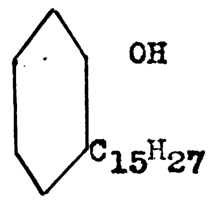
Harvey (26) obtained a product suitable for waterproofing walls by reacting the oil with barium hydroxide and then a glyerride.

Pillay (27) in 1935 found the formula of anacardic acid to be $C_{22}H_{32}O_3$ M.P.22.5° C. It contained two active hydrogens one of which was phenolic. Pyrolysis of the acid yielded anacardol $C_{21}H_{32}O$ B.P. 215.2°, d^{30}_{30} .9399 n^{30} 1.5107. Two double bonds were shown in both compounds, but were not located. The side chain however was straight.

The formula.



Anacardic acid



Anacardol

Rector (28) developed a new process for extracting the oil from the shell in 1936. The nuts were immersed in a bath of cashew nut shell oil at a temperature and for a time adjusted to effect the discharge of a major portion of the oil without scorching the kernels.

Patel (29) in 1937 studied the effects of decarboxylation. The saponification number (117) and acid value (109) of the oil decreased on heating until they became almost zero. The rate of decrease was higher at higher temperatures. This decrease was due mainly to decarboxylation. On heating the iodine value (266) increased initially owing to the splitting off of carbon dioxide and the decomposition of the oil into unsaturated substituents. A subsequent decrease was thought to be due to polymerization of the unsaturates. The specific gravity (.996) of the oil decreased and then increased slightly on further heating. The mean molecular weight decreased to a minimum and then gradually increased.

Hughes (30) modified his previous method for the extraction of the oil by first causing the nut to absorb water and then immersing it in a hot bath of the shell oil. Harvey and Damitz (31) in 1937 patented a process for effecting the polymerization of the oil by using sulfuric acid. In 1938 Harvey and Damitz (32) devised a method of driving off the sulfur existing in the oil and then effecting polymerization.

In 1938 we found the first mention of cardanol (33) being used with formaldehyde. It was obtained by either steam distillation or distillation at atmospheric pressure.

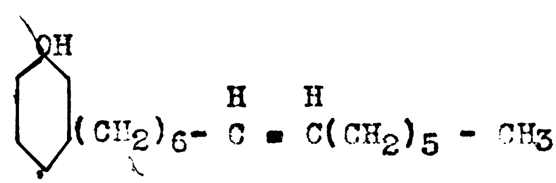
Gardner (34) in 1938 reported the use of cashew nut shell oil as a drying agent in paints.

Jeffries (35) also in 1938 reported another method for the extraction of the oil. A column of nuts and broken shells was subjected to a downward stream of superheated steam, the water and oil being collected at the bottom. In the same year Jeffries and Pierce (36) devised a special pretreatment of the nuts before extraction of the oil.

A patent issued to the Harvel Corporation (37) in 1938 described a process for the polymerization of cashew nut shell oil by using 1 - 6% by volume of concentrated sulfuric acid or with zinc chloride or tein tetrachloride. The product obtained was used in paints, varnishes and impregnants.

Wats and Bharacha (38) used the oil as a mosquito larvicide in 1938. Five parts of cashew nut shell oil and 95 parts of kerosene were used. In 1938 Pierce and Jeffries (39) added another revision to their apparatus for the extraction of the oil. This consisted in apparatus for effecting rapid cooling and draining of the shells that had been extracted.

Harvey (40) in 1939 showed the formula of cardanol to be $C_{20}H_{32}O$.



and used it with formaldehyde to make coatings, molded products, etc.

Hughes (41) in the same year polymerized cashew nut shell oil with glycerol phtholic anhydride condensation products to obtain materials suitable for sheeting and molding. Kiezmick (42) polymerized the oil with sulfuric acid to a flowable state and then completed polymerization to a rubbery state with hexamethalene tetramine.

Patel and Patel (43) reported that the roasted shells contained 18 - 20% oil with a saponification number of 4.5, iodine number of 294, d_{29} .9578 and mean molecular weight of 340.

Caplan (44) in 1940 used diethyl sulphate dissolved in the oil and heat to effect reaction of the solution with the metals naturally present in the oil. These precipitated metals were then removed and the product polymerized to yield resins suitable for paints, varnishes, etc.

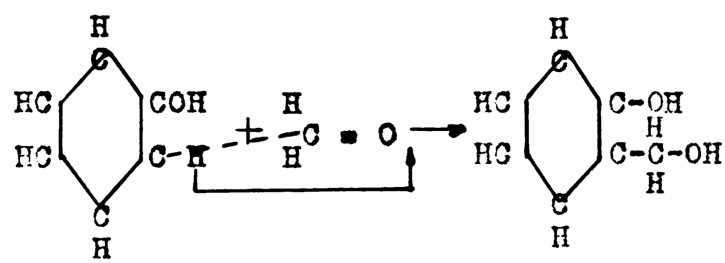
Downing (45) showed that dermatitis from cashew nut shell oil is not caused by ingestion of the cooked nuts, but only by contact with the oil of the shells and reported that ointments and pastes should be avoided but hot wet dressing applied.

Cayo (46) decreased the poison ivy effect by treating the oil with protein such as egg or blood albumin or heating with acetamide, benzamide, etc.

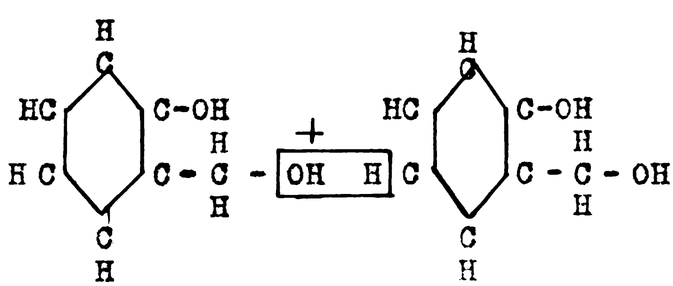
Harvey and Caplan (47) published a paper on cashew nut shell oil describing the manufacturing processes, polymerization utilizing both the unsaturated nature of the oil and the phenolic group. Upon distillation the distillate consisting largely of anacardic acid polymerized slowly. The residue showed both phenolic and unsaturated properties and also reacted slowly with aldehydes.

III. THEORETICAL

From the graphic formula on the following page it is evident that the components of cashew nut shell oil (cardanol and anacardic acid) and their synthetic derivatives (dihydrocardanol, anacardol and tetrahydroanacardic acid) are all substituted phenols and should therefore react as such in the presence of formaldehyde. According to Baekeland one mole of formaldehyde reacts with one mole of phenol or its derivatives to yield benzyl alcohols as follows:-

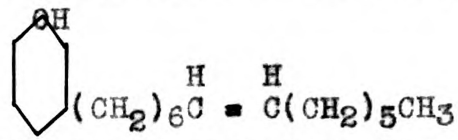
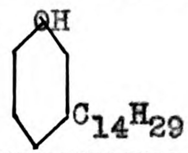
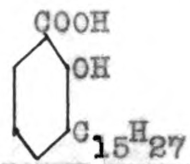
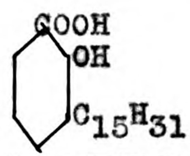
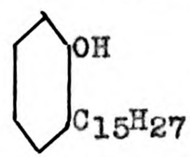


The benzyl alcohols formed will then, by the elimination of water, combine to give a straight chained, thermosetting resin



If however more formaldehyde is used, a thermosetting resin will be obtained due to the formation of cross linkages. All reactions carried out for this paper were

TABLE OF PHYSICAL CONSTANTS

Name	Formula	Melting Point	Boiling Point
Cardanol		-	225°/10 mm.
Dihydro Cardanol		50.5°	380° atmospheric 240°/10 mm.
Anacardic Acid		22.5°	-
Tetrahydro Anacardic Acid		92.5	-
Anacardol		-	215/14 mm. 205°/4 mm. 185°/3 mm.

mole per mole.

The speed of the reaction of the substituted phenols and formaldehyde varies with the position of the alkyl group in respect to the hydroxyl group. For instance, the reaction of meta xylene and formaldehyde is faster than phenol and formaldehyde and yields a thermosetting resin providing enough formaldehyde is present. This is due to the fact that both the hydroxyl and alkyl groups are ortho-para directing and consequently direct to the same positions on the ring.

With ortho and para xylenes the reaction is slower than phenol formaldehyde and only thermoplastic resins can be obtained because one position either ortho or para to the hydroxyl is blocked leaving two open.

In the case where an alky is substituted on both ortho positions or on one ortho and the para position the reaction is much slower than either of the above because only one position remains open. Only thermoplastic resins can be obtained from this type of phenol due to the fact that no cross linkages whatever can be formed.

Applying the above generalizations to the constituents of cashew nut shell oil, we should expect that cardanol, which is a meta substituted phenol, should react the fastest, anacardol (ortho substituted phenol) next and anacardic acid (di ortho substituted phenol) the slowest. The raw oil which is predominantly cardanol should probably react between anacardol and anacardic acid. By glancing at the time of reaction for each of the above on Tables I, II, III, and IV we find these expectations correct.

IV. TECHNIQUE OF HANDLING THE OIL

The first and foremost consideration in handling the oil is scrupulous cleanliness. The oil should be stored in a place where miscellaneous contact is not apt to occur. Persons handling the oil should develop a technique toward it which may be described as similar in thorough cleanliness to that used in handling virile bacteria. This does not mean, however, that the operator need be afraid of the material or should hesitate to get it on his hands, because only those who are not allergic should work with the oil. The point to emphasize is that minute traces of the oil, spread through careless handling, can cause very unpleasant effects to people unaware of its presence. To be specific, traces of the oil left on door knobs or table tops can poison individuals who have nothing to do with the problem. The essential thing is for the operator to wash his hands very frequently, and at the slightest provocation, with plenty of mild soap and lukewarm water. A generous supply of paper towels should be near at hand, not only to wipe the hands but also to wipe containers and benches when the oil is transferred or spilled. The used towels should be deposited in paper sacks and burned, helping to prevent the spread of the oil.

Apparatus heavily contaminated should be first soaked in a suitable solvent such as ethylene dichloride. Ethyl acetate can also be used satisfactorily. Beyond this, washing or scrubbing with soapy water is generally sufficient to clean up the apparatus and make it fit for future use.

During the previous eleven months only one case of poisoning has occurred. This was traced to the common sink used by every one in the laboratory. The only way to eliminate poisoning from this source, if the preceeding precautions have been carried out, is to have a separate sink for washing contaminated dishes. If this is impossible, the sink should be used as infrequently as possible and should be scrubbed thoroughly with soap and lukewarm water after washing dishes containing the oil. A private stock of brushes and soap powder is also recommended. The trouble seems to be worse in hot weather when the pores of the skin are naturally open. Contaminated clothing should be sponged with solvent and the garment thoroughly washed or dry cleaned before being worn again.

There appears to be some justification for the belief that the use of grease or oil on the hands moderates the toxicity of the oil. The action seems to be purely one of delaying adsorption into the lower layers of the skin and facilitating the washing off of the contamination. An individual doing much dishwashing should protect the skin by use of some ointment or vanishing cream.

The better the condition of the skin the less likely the chance for irritation. In acute cases "Calamine Lotion," freely applied, is a good remedy. This laboratory, however, has found that "Burrow's Solution" is much superior to "Calamine Lotion." Burrow's solution is made by dissolving 150 grams of lead acetate and 85 grams of aluminum sulphate in one liter of water. The effected area should be kept moist with the solution by applying dressings saturated with the solution.

Because of the fact that cashew nut shell oil has such a serious affect upon some individuals only those persons who are not allergic should work with it. A very simple way to determine whether or not an individual is allergic is to place a small drop of the oil (no more than the amount that will adhere to the point of a pin) on the wrist. After a minute the excess is wiped off and a bandage applied. If the patient is allergic the spot will begin to itch within 12 to 18 hours and a large red blotch will appear. As soon as the positive signs appear apply Burrow's Solution or Calamine Lotion as directed above. If nothing develops within two days the test is taken as negative.

V. EXPERIMENTAL

A. Materials

Cashew nut shell oil was furnished by the General Foods Inc. and used as such without further purification.

Calcium anacardate was prepared by adding a solution of cashew nut shell oil in isopropyl alcohol to a water suspension of slaked lime.

Isopropyl alcohol (practical B.P. 82-83°C) was purchased from Eastman Kodak Co.

Slaked lime (commercial) was obtained from Carrier Stephens Co.

Cardanol was obtained by evaporation of the solvent from which calcium anacardate had been precipitated and removed.

Anacardic acid was prepared by adding sulfuric acid (1-8 solution) to a suspension of calcium anacardate in hexane.

Hexane (practical B.P. 68-70°C) was purchased from Eastman Kodak Co.

Anacardol was obtained by the decarboxylation of anacardic acid.

Formalin (40% commercial) was the source of formaldehyde.

Acetaldehyde, a Central Scientific product, was used after distillation at 25°C.

Chlor acetone, a Commercial Solvents product, was used after distillation at 119°C.

Phenol (U.S.P.) was obtained from Carrier Stephens and used after distillation at 184°C.

Linseed oil (Commercial, boiled) was obtained from Carrier Stephens.

B. Separation of the Component Parts.

1. Preparation of Calcium Anacardate

Five hundred grams of centrifuged cashew nut shell oil were dissolved in three liters of isopropyl alcohol, shaken at regular intervals and allowed to stand overnight. The precipitate formed was removed by centrifuging.

One hundred and eight grams of slaked lime were triturated to a thin paste with a sufficient quantity of water added in small quantities.

The lime paste was then transferred to a five liter, three neck, round bottom flask fitted with an efficient stirrer, reflux condensor and dropping funnel and suspended in 1000 c.c. of isopropyl alcohol. To this suspension the centrifuged oil was added in a small stream from the dropping. The mixture was stirred until the reaction appeared to be complete and then for an additional hour. The completion of the reaction was indicated by the reduction in the color of the solution from dark brown to a light reddish brown and by the formation of a rather voluminous light red colored, finely divided precipitate.

At the completion of the additional stirring, the mixture was filtered by suction, washed with fresh solvent, pressed dry, and then allowed to dry in the air. The yield of solvent free salt was approximately 80% of the weight of the cashew nut shell oil used. According to this, disregarding the original precipitate filtered off, there was approximately 82% acid and 28% cardanol in the cashew nut shell oil.

The time of reaction varied from one hour and forty minutes to twenty-four hours, the usual time being about four to five hours. The time of reaction appeared to be dependent, to a considerable extent, upon the amount of water in the system. More water seemed to favor the reaction while a dry solvent decelerated it. The reaction was also accelerated by heating the mixture on a water bath, using the reflux condensor to minimize solvent loss.

2. Isolation of Cardanol

The preparation of cardanol, due to the fact that it is soluble in isopropyl alcohol, simply involved the isolation of it from the filtrate obtained in the preparation of calcium anacardate.

The filtrate obtained from the preparation of calcium anacardate was centrifuged to make sure all the Ca. anacardate was removed. The solution was then placed in a one liter claisen flask and the isopropyl alcohol removed over a water bath. When most of the alcohol was removed, the residue was taken from the flask, a new portion added and the distillation repeated. All the residues were then placed back in the flask and the remaining alcohol removed by heat from the water bath and gentle suction. This procedure was found to be faster and more efficient than adding more solution to the flask as the solvent was removed. When foaming began, which was an indication that only traces of solvent remained, the residue was placed in an 80°C oven to remove the last traces of solvent. The cardanol was used in this form and also in the purified form. The pure product boils at 225°C/10 mm.

3. Regeneration of Anacardic Acid

Four hundred grams of air dry calcium anacardate were placed in a five liter three neck round bottom flask equipped with a mechanical stirrer, reflux condensor and dropping funnel. Three liters of hexane were added and the suspension stirred vigorously. The quantity of sulfuric acid equivalent to the calcium present as determined by ash analysis was diluted with eight parts of water and added slowly but continuously from the dropping funnel. The amount of sulfuric acid used usually amounted to about 90 c.c. specific gravity 1.84. The stirring was continued for two hours after the last of the sulfuric acid had been added. The supernatent liquid was then decanted as completely as possible and the residue washed with hexane to remove any adhering anacardic acid, the washing being combined with that obtained by decantation. The calcium sulfate was centrifuged. The liquid layer (hexane containing sulfuric acid was placed with the previously obtained liquid and the remainder was discarded. The hexane layer of the reaction was also centrifuged to remove any calcium sulfate present, and then washed with water until the latter was neutral to litmus paper. It was found advantageous to be very careful and shake the hexane-water mixture gently in order to avoid the formation of emulsions which were difficult to break. These emulsions when once formed could only be broken by centrifuging.

The washed hexane solution was transferred to a distilling flask provided with a condensor and automatic separator whereby the water was removed from the system and the hexane recycled. This operation was continued until the anacardic acid was free from water and then recovered by distilling off the hexane. The last portion of solvent was removed under a slight vacuum with a stream of air bubbles passing through the liquid. This was tried on cardanol but yielded a polymerized product so the alternate method as previously described was adopted. Anacardic acid in the pure form is a solid melting at 22.5°. Purification could not be carried out by distillation even at reduced pressure because it is so easily decarboxylated. The acid used for making resins was that obtained in the crude state after all hexane had been removed.

4. Preparation of Anacardol

Anacardol was prepared by the decarboxylation of anacardic acid. The decarboxylation was carried out by mixing one percent of finely divided slaked lime with any desired quantity of acid. Usually 200 grams of acid and 20 grams of slaked lime were used. The mixture was heated to a temperature of 125-150°C, preferably 130-140°, until the evolution of carbon dioxide had substantially ceased. The heating time varied between two and four hours depending upon the rate of heating and other mechanical circumstances. The reaction was carried out in a round bottom flask or a distilling flask. When the former was used it was fitted with a still head for vacuum distillation of the reaction product. This operation was conducted under a vacuum of 10 mm. or less. The still head had to be insulated against heat loss and superheating kept at a minimum. The chief difficulty was foaming which became troublesome at the time the vacuum was applied or as the temperature was raised above the initial to effect distillation. The foaming was due to sudden evolution of carbon dioxide that was held in the oil, or that was liberated as the reaction reaches completion. The stability of the foam is largely conditioned by impurities in the anacardic acid carried over from the cashew nut shell oil. Anacardol boils at 185-187°C at 3 mm. and $n_D^{25} = 1.5090$.

Another procedure for decarboxylation was developed. Two hundred grams of the acid and twenty grams of slaked lime were placed in a two liter, three neck, round bottom flask fitted with a condensor, thermometer and stirrer. The temperature was hold between 130-140°C for six hours while the mixture was stirred to help liberate the carbon dioxide without causing too much foaming. The temperature was then raised to 170° for an hour, the mixture cooled, centrifuged and used either in this form or after further purification by distillation. Use of the cardanol in this crude state was justified by the fact that neither the raw oil nor the acid were used in the pure state. The pure anacardol was a yellow liquid boiling at 185-187° at 3 mm.

C. Separation of the Components by Distillation.

Harvey (23) in 1934 reported a method for the distillation of cashew nut shell oil at atmospheric pressure which yielded a product boiling between the temperatures of 300-400^{o}C. In 1938 steam distillation was also mentioned as well as vacuum distillation. All three processes were covered by patents, however, so no definite information or procedure was obtained. As a result distillation at atmospheric, in vacuum, or with steam ended in this laboratory in failure. The main difficulty was the large amount of foaming at high temperature due undoubtedly to decarboxylation of the acid and impurities. Several anti foam agents were used but none were found that would boil higher than the oil. Not much time was spent on this because the main object of the problem was formation of resin and also because the separation described in section B was very excellent.

D. Polymerization Reactions

The polymerization reactions were divided into four groups viz: the polymerization of (1) the whole oil, (2) anacardic acid, (3) cardanol and (4) anacardol. Since all reactions were carried out in essentially the same manner, only one will be described here.

One-eighth mole of polymerizable substance (either the whole oil or a component) was placed in a 500 cc flask equipped with a mechanical stirrer, thermometer and reflux condensor and stirred for a few minutes. One-eighth mole of formaldehyde (10 cc formalin) and 1 cc of 1% sodium hydroxide were added and the temperature raised to 88-92°C until the reaction was complete. When no modifier was used the polymerizable substance and the formaldehyde were equimolecular in quantity. The sodium hydroxide catalyst was a 1% solution and the volume added equalled 10% of the volume of formalin used. When the reaction mixture assumed a taffy-like appearance and adhered to the rotating stirring rod rather than the bottom of the flask gentle suction was applied to remove any excess water. The dehydrated product was then poured into tins and baked at 50° for 36 hours. All heat was applied by an oil bath rather than a burner to prevent sectional overheating and scorching.

In cases where phenol was used as the modifier the amount of formaldehyde added was equal to the total number of moles of the polymerizable substance and the phenol. For instance 1/4 mole of formaldehyde was added to a mixture of 1/8 mole of oil and 1/8 mole of phenol. The catalyst as mentioned above would be 10% of the volume of formalin or 2 c.c.

This policy differed, however, when linseed oil was used as the modifier in that the amount of formaldehyde used was equivalent only to the molecular quantity of the polymerizable substance regardless of the quantity of the linseed oil added.

The end point of the cardanol, formaldehyde reaction differed from the one described above in that instead of becoming taffy-like, it became solid and assumed the appearance of curd.

The following reactions were carried out with all four groups. The quantity of the polymerizable substance was kept constant (1/8 mole) while the modifiers, polymerizing agents, catalysts and conditions were varied. No quantities will be given but they are tabulated in the tables, pages 35-38.

Modifiers

Phenol

Linseed Oil

Polymerizing Agents

Formaldehyde

Acetaldehyde

Acetone

Chloracetone

Catalysts

Sodium Hydroxide (1%)

Hydrochloric Acid (1%)

Acetic Acid (1%)

The only reaction carried out differently from the above procedure was that of anacardic acid, urea and formaldehyde.

One-eighth mole of anacardic acid and one-eighth mole of urea were placed in a flask similar to the above. The mixture was stirred and heated for 9½ hours. One-quarter mole (19 cc) of formaldehyde and the proper amount of catalyst were added and the reaction brought to the usual end point. The dehydrated product was allowed to bake at 50° for the usual 36 hours. This reaction was also carried out with one-eighth mole of acid, one-sixteenth mole of urea and three-sixteenths mole of formaldehyde.

E. Stabilization of Color.

The resins formed from the whole oil, anacardic acid and anacardol turned black on standing in air while those from cardanol turned from red to black and back to red. It was thought at first that this was due to impurities in the oil. Resins, however, obtained from purified oil turned black also, so another solution such as oxidation of the unpolymerized double bonds was turned to. An attempt to inhibit this oxidation was made by adding an anti-oxidant or inhibitor such as hydroquinone. This did not prevent the blackening, but stimulated it and the resins obtained darkened more quickly than those with no hydroquinone in them.

Still working on the belief that the double bonds were responsible for the darkening, addition of HCl and hydrogen was tried next. Dry HCl gas was passed into an anhydrous solution of cashew nut shell oil in isopropyl alcohol. The product obtained after careful evaporation of the solvent polymerized very rapidly and the resin obtained also darkened. The hydrogen chloride product upon distillation gave up hydrogen chloride at a low temperature showing that the HCl did not add to the double bond but was probably only dissolved in the oil.

Hydrogenation was carried out in the apparatus on page 31 with molecular hydrogen in the presence of platinum oxide. No hydrogenated products were obtained. This failure was probably due to that fact that no heat could be applied to the apparatus and only very little pressure.

Preparation of the Platinum Catalyst.

Three and one-half grams of platinum chloride were placed in a porcelain casserole and 10 cc. of water and 35 g. of C. P. sodium nitrate were added. The mixture was evaporated to dryness over a Bunsen burner and stirred continuously. The temperature was raised to 350°-370°C in about ten minutes. Fusion took place and brown fumes were evolved while the precipitation of brown platinum oxide gradually took place. During this operation foaming occurred, which was controlled by more vigorous stirring and an additional burner directed at the top of the casserole. At the end of 15 minutes, when the temperature had reached 400°C, the evolution of gas greatly decreased. The temperature was held at this point until the evolution of gas had ceased and then heated for thirty minutes longer. The mass was allowed to cool and was then washed with water. The washings were stopped as soon as the precipitated began to become colloidal.

Procedure for Use of Apparatus Used.

Ten grams of oil, .2 g. of platinum oxide and 200 c.c. of 95% ethyl alcohol were placed in the reaction bottle. The mercury bulb was placed at position A with stopcock D closed and E open to evacuate the system. Stopcock C was opened and an even flow of hydrogen obtained through the beaker of water. E and C were closed and D opened to allow the hydrogen to fill the system. After the evacuation and charging was repeated several times to insure a system free from air, stopcocks E and D were closed, the hydrogen source shut off and the mercury reservoir placed at position B to give a slight pressure. More hydrogen was added to the system at frequent intervals and recorded to see if a quantitative addition could be made.

Before charging the reactor the system was tested for leaks by filling with hydrogen to a slight pressure and noting any change in the mercury level.

See Diagram II, page 31

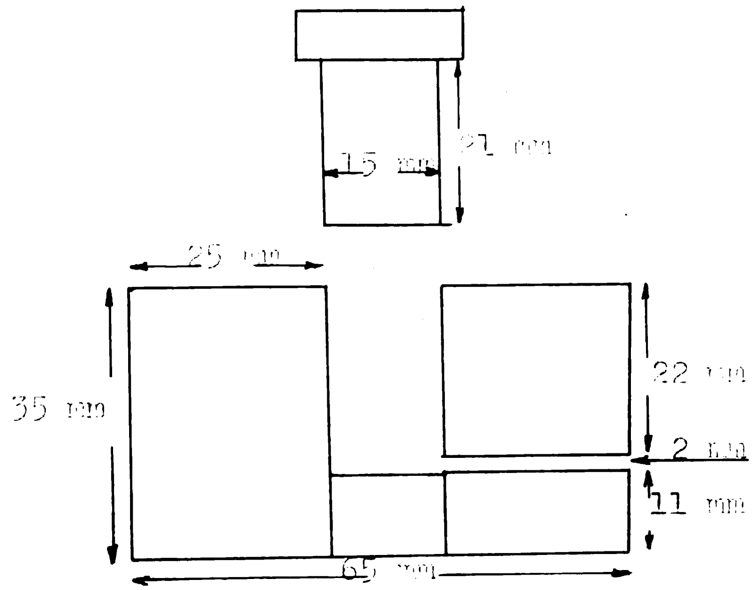


DIAGRAM 1

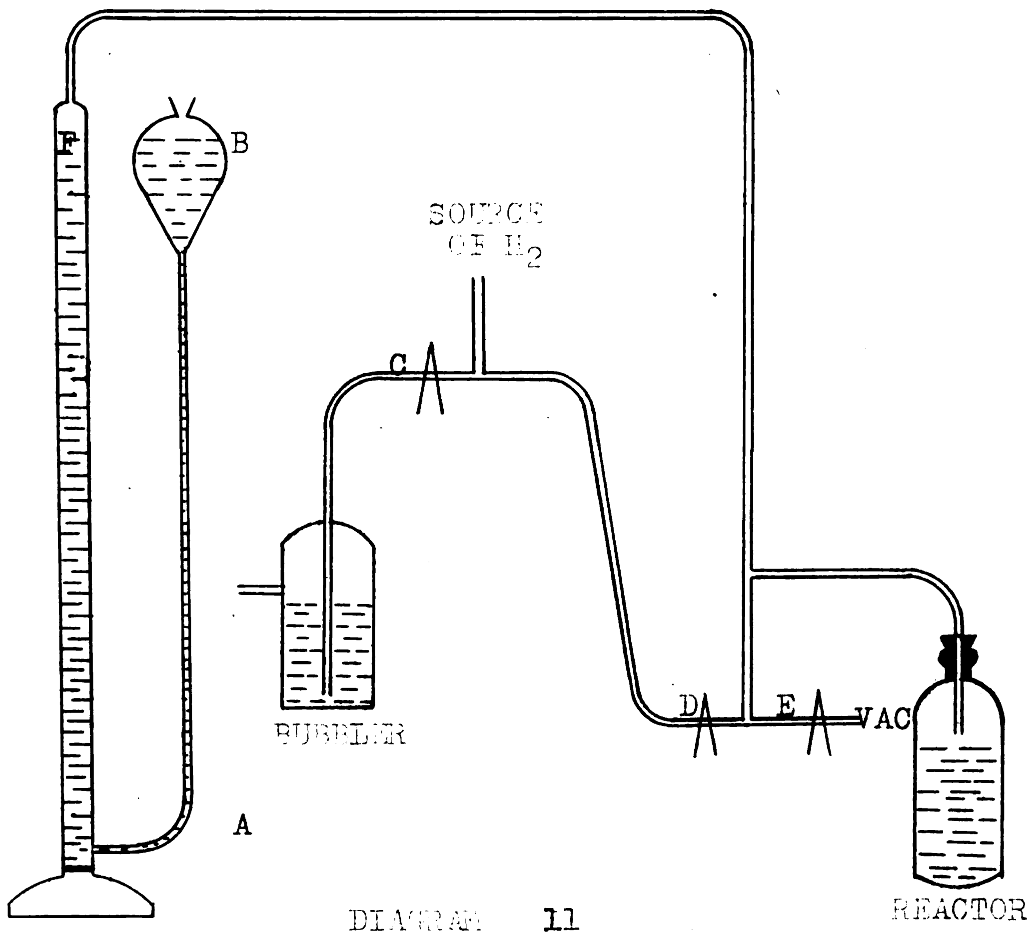


DIAGRAM 11

VI. PHYSICAL PROPERTIES OF RESINS

The following observations and tests were carried out on the resins obtained in order to determine the effect of various catalysts, modifiers and polymerizing agents and to note any similarities or dissimilarities produced by varying the above.

A. Observations

1. Time -- The time of reaction can hardly be classified as an observation but nevertheless gives valuable information regarding effect of catalysts, modifiers and polymerizing agents.

2. Color -- All resins obtained were of the same general brown color.

3. Color stability -- Darkening took place erratically in all resins and no attempt will be made to explain it. Stabilization of color was attempted (see page28) with no success. Neither color nor color stability are very definite because they depend upon personal opinion rather than on results obtained mechanically as do the following.

B. Testing

1. Softening Point

The apparatus used was a Fisher melting point apparatus. A pyramid 1 mm. square at the base and 1 mm. high was cut from a piece of fresh, undarkened resin and placed on the bottom cover glass. This was covered with a transparent weight of 3.807 grams and heat slowly applied. The softening point was taken at the temperature at which the sides of the pyramid began to buckle.

2. Melting Point

A pyramid of resin one mm. square at the base and 6 mm. long was cut from a fresh piece of unhardened resin. A crucible was heated and the point of the pyramid stuck to the bottom of the inside just tightly enough so it could not be shaken loose. The resin was then covered with mercury, a thermometer inserted and heat applied. The melting point was that point at which the resin rose to the surface of the liquid. Melting points were repeated until checks within three degrees were obtained.

3. Flow

Fine pieces of unhardened resin were placed in the cup of the mold shown on page 31. The top of the mold was placed into position, the whole mold put between the platens of an hydraulic press and pressure applied. The pressure at which the resin emerged from the small opening was taken as the flow pressure.

In cases where flow was taken at elevated temperatures the resin was placed in the cold mold and then the temperature raised. When the temperature of the mold became correct, pressure was applied.

4. Specific Gravity

A cubic centimeter of resin was cut from a piece of unoxidized resin and weighed both in air and water. Subtracting the weight in water from the weight in air and then dividing this number into the weight in air gave the specific gravity. Specific gravity was calculated to the third place and repeated until a check of five parts on the third place was obtained.

It was at first believed that specific gravity would be quite valuable in determining degree of polymerization. From Chart I, however, it can be seen they fall very haphazardly; therefore specific gravity was not run on other samples.

CHART I. - Reaction of Cashew Nut Shell Liquid

No.	Grams C.N.S.L.	Modifier	Grams Mod.	Polym. Agent	Amount Agent cc.	Catalyst	Vol. Cat. cc.	Time hrs.	Physical State	Softening Point	M.P.	Color	Oxidation	Flow 23° C.	Sp. Gr.
A	43	--	--	--	--	NaOH	1	20	Liquid	--	--	Brown	--	--	--
B		--	--	HCHO	10	--	--	3-1/2	Soft solid	59	81	2	2	2750	1.148
C		--	--		10	NaOH	1	3		75	88	3	3	3250	1.118
D		--	--		10	HCl	1	2-1/2		71	86	Darkest brown 4	Least 1	2250	1.146
E		--	--		10	CH_3COOH	1	2-3/4		52	73	Lightest brown 1	Most 4	1500	1.136
F		Phenol	2.9		11.7	NaOH	1.17	4-3/4		69	78	Darkest brown 3	Most 3	2500	1.123
G		"	5.9		14.1		1.41	6-1/2		62	84	2	2	2250	1.159
H		"	11.7		19.0		1.9	10-3/4		53	92	Lightest brown 1	Least 1	2000	1.154
I		Linseed oil	2.5		10		1	3-3/4		49	68	Darkest brown 3	Most 3	2750	1.151
J		"	5.0		10			5-1/4		44	65	2	2	1650	1.129
K		"	10.0		10			10-1/2		39	62	Lightest brown 1	Least 1	1150	1.131
L		"	20.0		10			13	Liquid	--	--	Dark brown	--	--	--
M		"	35.0		10			17		--	--		--	--	--
N		"	70.0		10			20		--	--		--	--	--
O		--	--	CH_3CHO	5.5			20		--	--		--	--	--
P		--	--	Acetone	5.5			20		--	--		--	--	--
Q		--	--	Cl Acetone	10			20		--	--		--	--	--
R		Hydroquinone		HCHO	10			4	Soft solid	58	85	Dark brown	Much	2750	1.178
S		Spec. Treated		HCHO	10			3	Soft solid	82	120	Light brown	Little	3250	1.150

CHART II. - <u>Reactions of Anacardic Acid</u>

Number	Grams Acid	Modifier	Grams. Mod.	Polym. Agent	Amount Agent cc.	Catalyst	Vol. Cat. cc.	Time hrs.	Physical State	Softening Point	M.P.	Color	Oxidation	Flow 23° C.
A	43	--	--	--	--	NaOH	1	40	Liquid	--	--	Brown	--	Most liquid
B		--	--	HCHO	10	--	--	40	"	--	--	"	--	2
C		--	--		--	NaOH	1	40	"	--	--	"	--	3
D		--	--		--	HCl	1	40	"	--	--	"	--	Most solid 4
E		Phenol	11.7		19	NaOH	1.9	31-1/2	Most rubbery 3	34	99	Black 3	Slight	1250
F		"	5.9		14.1		1.41	34-3/4	2	30	93	2	"	1000
G		"	2.9		11.7		1.17	38	Least rubbery 1	25	86	Brownish black 1	"	<1000
H		Linseed	2.5		10		1	40	Liquid	--	--	Brown	--	--
I		Urea	7.5	--	--		--	9-1/2	Sandy solid	--	98	Dark tan	--	Most solid 2
J		"	3.8	--	--		--	9-1/2	Sandy solid	--	45	Light tan	--	Least solid 1
K		"	7.5	HCHO	19.0		19	4	Tacky more 2	33	55	Black	Slight	1100
L		"	3.8	HCHO	14.1		1.4	6	Tacky less 1	29	45	Tan	Slight	<1000
M		--	--	CH_3CHO	5.5		1	40	Liquid	--	--	Brown	--	Most solid 3
N		--	--	Acetone	5.5		1	40	"	--	--	"	--	1
O		--	--	Cl Acetone	10		1	40	"	--	--	"	--	2

CHART III. - Reactions of Cardanol

No.	Grams Cardanol	Modifier	Grams Mod.	Polym. Agent	Amount Agent cc.	Catalyst	Vol. Cat. cc.	Time	Physical State	Softening Point	M.P.	Color	Oxidation	Flow 23° C.	Flow 100° C.
A	36	--	--	--	--	NaOH	1	hrs. 5	Liquid	--	--	Brown	Slight	--	--
B		--	--	HCHO	10	--	--	min. 12	Granular	175	--	Dk. red Brown		7500	3000
C		--	--		10	NaOH	1	min. 4	Granular	240	--	Yellow Brown		8000+	8000
D		Phenol	3		1.17		1.17	min. 5	Flaky	156	--	M. red Brown		6750	2500
E		"	5.9		1.41		1.41	min. 7	Flaky	141	--	Lt. red Brown		6000	2250
F		"	11.8		19.0		1.9	min. 9	Flaky	122	--	Dk. red Brown		5250	2000
G		Linseed	35		10		1	min. 12	Granular	81	--	Dark Red		3000	50° 1500
H		"	50		10		1	min. 15	Granular	65	--	Med. Red		1500	1000
I		"	100		10		1	min. 17	Granular	58	--	Light Red		<1000	<1000
J		"	100		5		1	min. 30	Soft	40	--	Red		<1000	<1000
K		--	--	CH_3CHO	5.5		1	hrs. 5	Liquid	--	--	Brown		--	--
L		--	--	Acetone	5.5		1	hrs. 5	Liquid	--	--	Brown		--	--
M		--	--	Cl Acetone	10		1	hrs. 5	Liquid	--	--	Brown		--	--

CHART IV. - <u>Reactions of Anacardol</u>

No.	Grams Anacardol	Modifier	Grams Mod.	Polym. Agent	Amount Agent cc.	Catalyst	Vol. Cat. cc.	Time hrs.	Physical State	Softening Point	M.P.	Color	Oxidation	Flow 23° C.
A	37.5	--	--	--	--	NaOH	1	5	Liquid	--	--	--	--	--
B		--	--	HCHO	10	--	--	2:25	Pliable more 2	72	--	Dark tan	Slight	2250
C		--	--		10	NaOH	1	1:20	Pliable less 1	78	--	Tan	Slight	2750
D		Phenol	3		11.7		1.17	1:35	Rubbery more 3	70	--	Black	Hardens	4000
E		"	5.9		14.1		1.41	2:00	2	65	--	Brown black	Hardens	3750
F		"	11.7		19.0		1.90	3:05	Rubbery less 1	60	--	Brown	Hardens	5500
G		Linseed	10		10		1	3:20	Tacky	20	--	Tan	Slight	<1000
H		"	35		10		1	4:20	Tacky	20	--	Black	Slight	<1000
I		"	50		10		1	5	Liquid	--	--	--	--	--
J		"	100		10		1	5	Liquid	--	--	--	--	--
K		--	--	CH_3CHO	5.5		1	5	Liquid	--	--	--	--	--
L		--	--	Acetone	5.5		1	5	Liquid	--	--	--	--	--
M		--	--	Cl Acetone	10		1	5	Liquid	--	--	--	--	--
N		--	--	HCHO	10	HCl	1	1:10	Pliable	74	--	--	--	--

VII. CONCLUSIONS

A. Cashew Nut Shell Oil

1. C.N.S.O. will polymerize with formaldehyde alone, but a catalyst speeds the reaction considerably.

2. Increasing the amount of phenol slows the reaction, causes a decrease in softening point and flow pressure but increases the melting point and improves color stability.

3. Increasing the amount of linseed oil also slows the reaction and causes a decrease in softening point, melting point, flow pressure and improves color stability.

4. C.N.S.O. will not polymerize with acetaldehyde, acetone or chloracetone.

B. Anacardic Acid

1. Anacardic acid cannot be polymerized with formaldehyde, acetaldehyde, acetone or chloracetone even in the presence of a catalyst.

2. Addition of phenol gives a solid resin. Increasing the amount of phenol increases the speed of reaction, melting point, softening point and flow pressure. It imparts a rubberyness to the product.

3. Addition of linseed oil has no effect.

4. Addition of urea gives a tacky resin. Increasing amount of urea yields a resin less tacky with an increased melting point, softening point and flow pressure.

C. Cardanol

1. Cardanol polymerizes rapidly with formaldehyde and catalysts speed the reaction.

2. Increasing the amount of phenol slows the reaction and decreases the softening point, melting point and flow pressure.

3. Increasing the amount of linseed oil slows the reaction and decreases the softening point, melting point and flow pressure.

4. Cardanol will polymerize slightly with acetaldehyde but not with acetone or acetaldehyde.

5. Increasing phenol deepens color, while increasing linseed oil lightens color. Color stability is good.

D. Anacardol

1. Catalysts again speed the reaction.

2. Increasing the amount of phenol slows the reaction and decreases the softening point and flow pressure.

3. Linseed oil also slows the reaction and decreases the softening point and flow pressure.

4. Anacardol will not react with acetaldehyde, acetone or chlor acetone.

Generally it can be stated that the speed of the reactions take place in the following order, the first being the fastest.

1. Cardanol

2. Anacardol

3. Cashew Nut Shell Oil

4. Anacardic Acid

Phenol increases the speed of the anacardic acid reaction but slows the reactions of Cardanol, Anacardol and C.N.S.O. Linseed oil slows the reaction in all four cases.

VIII. SUMMARY

1. Cashew Nut Shell Oil was separated into its components, namely, anacardic acid and cardanol.

2. Anacardic acid was decarboxylated to yield anacardol.

3. These four oils were then polymerized with various polymerizing agents, catalysts, modifiers and conditions.

4. The products obtained were tested.

5. An attempt to improve color stability was made.

6. Conclusions were drawn from Charts I-IV.

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