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The Utilization of Hydrogenated Tall Oil in Paper Furnishes

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THE UTILIZATION OF HYDROGENATED
TALL OIL IN PAPER FURNISHES /

Submitted to Dr. R. A. Diehm
In Fulfillment of Course No. 571
Research Problems in Pulp and Paper
Western Michigan University

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Abstract

A literature survey is presented concerning the properties of tall oil, the theory of catalysis, and catalytic hydrogenation applied to tall oil. It is the purpose of the experimental work to prepare a material from tall oil by hydrogenation which will lend itself more useful as a sizing agent for certain low grades of paper.

The experimental results indicated that by hydrogenating tall oil soap, a whiter, less oily material is obtainable. Handsheets were prepared using this hydrogenated material, the starting material, and rosin size as sizing agents. It was found that the handsheets sized with the hydrogenated material had a higher brightness than those sized with the non-hydrogenated tall oil soap. The strength of sizing of the hydrogenated versus the non-hydrogenated sized paper was not appreciably changed.

Acknowledgements

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LITERATURE SURVEY

The Utilization of Hydrogenated Tall Oil In Paper Furnishes

INTRODUCTION

Throughout the history of the kraft pulping process, tall oil soap skimmings have been obtained from the black liquor, although it wasn't until after the turn of the century that the value of this material was recognized and made commercially available. Recently, there have been vast quantities of work performed in attempts to try and more economically utilize this inexpensive source of raw materials.

It is the objective of this investigation to prepare a useful product for the paper industry from tall oil by hydrogenation. Since there is generally an abundant supply of tall oil around most kraft mills, it might be desirable to utilize this wood by-product right at the mill site.

Much of the rosin size consumed by the paper industry originally comes from tall oil. Since tall oil is about half rosin, it seems logical that this material may yield itself effective in sizing certain grades of kraft papers. The literature cited revealed a case in Sweden where precisely this had been done, although the tall oil size produced here was only 60-65 per cent as effective as pure rosin size (1). When added to the extent of giving sizing

qualities equal to rosin size, the brightness and strength of the tall oil sized paper was appreciably lowered (13). This fact put heavy limitations on the use of tall oil size.

It has been proposed by the writer that by hydrogenating tall oil, a whiter, less oily material with better sizing properties may be obtained. It is hoped that the properties of such a material will more closely resemble those of rosin size so that the warrant of its use would make the hydrogenation process economically feasible.

It is beyond the scope of this investigation to attempt to suggest an economically feasible method for the production of a hydrogenated tall oil size.

The literature which follows includes a rather inclusive description of tall oil and brief resumé's on the theory of catalysis, catalytic hydrogenation, and catalytic hydrogenation applied to tall oil. It is the writer's intent that the reader will gain sufficient knowledge from the literature survey to understand the problem at hand.

TALL OIL SURVEY

Tall Oil - Defined: Tall oil is "the natural mixture of rosin acids related to abietic acid and of fatty acids related to oleic acid, together with non-acidic bodies, which is obtained by acidifying the black liquor skimmings of the alkaline pulping process." Tall oil is obtained entirely from the black liquor of the kraft process of wood pulp manufacture, using resinous woods such as pine (29).

The name tall oil was derived from the Swedish "tallolja" (literally, "pine oil") and was adopted after the term "liquid rosin" (from the German flüssige borz) and had been prohibited under the Harrison Naval Stores Act. Pine oil is a different product in the United States (chiefly α - terpinol) (29).

Since it is the cheapest suitable organic material available, tall oil is being used in increasing amounts in applications in which the resin acids present in the tall oil are either used or can be tolerated.

Tall Oil History (25): The history of tall oil is relatively short. Records state that commercial interests probably began in Sweden about the beginning of the twentieth century. It has been estimated that the product was first marketed

around 1903. In the United States, late in 1910, William J. Hough began marketing tall oil skimmings from a new \$30,000 plant in Elkton, Maryland. He also patented a process for acidifying these skimmings to form "free rosin."

Until rather recently, the general practice for the collection and acidification of the tall oil soap was to provide some means for skimming the salted-out material which floated to the surface of the black liquor at practically any concentration and conveying it to a collection tank where a further separation could be made. The concentrated soap was then either pumped to tank for sale or was sent to a tall oil plant where it was cooked with sulphuric acid. In the latter case, the tall oil fatty and rosin acids were floated to the surface of the liquid and were collected and either shipped as such or sent to a refinery.

More recently there have been available facilities for a complete, continuous tall oil acidification plant in which all separable black liquor solids are removed prior to the acidification step. This final separation is accomplished by means of a super-centrifuge. As a result of the removal of black liquor solids before acidification, no lignin compounds are precipitated to absorb any of the oil produced. It is claimed that a higher yield results, together with more uniform low moisture content, and a lower sterol fraction in the finished product.

The removal of the soap from the black liquor before it

reaches the more concentrated effects in the evaporators resulted generally in improved evaporator operation. Further, if any attempt was made to burn the skimmings in the recovery furnace, the recovery operation would be adversely affected. Purely for these reasons, skimming took place in some plants with the result that the mill was confronted with this problem of disposal.

The advent of World War II with its enormous demands for fats served to point out the value of this product. For the first time, it became generally recognized that tall oil is the cheapest source of fatty acids in the world and one of its most abundant and stable. From this point on, the mill operator began seriously to interest himself in the collection of this valuable material. This resulted in his technical staff investigating ways and means to improve the collection of the skimmings and to obtain data pointing out the main factors contributing to better separation of the soap.

Description of Crude Tall Oil: The geographical location from which the wood is taken shows a marked influence on the composition of the tall oil. The factor of greatest importance here is the rosin/fatty acid ratio. Contrary to what may be expected, the season of the year in which the trees are harvested has little or no affect on the tall oil composition (21).

Crude tall oil, when free from gross contaminations (fiber, trash, etc.), shows in thin layers an orange-red color with

green fluorescence. The odor of tall oil is unpleasant and penetrating. The viscosity is variable, increasing with rosin acids content and also with material insoluble in petroleum ether. Physical tests commonly employed for vegetable oils do not give clearly defined values at low temperatures. Thus, crystallization of rosin acids is likely to occur before the sample can be cooled to the minimum temperature at which it will flow. Also, the titer test is quite low and not very reproducible (26).

The composition of crude tall oil follows closely with that of the ether extracts of the woods used to make pulp and varies with the species. Pines give higher yields with higher rosin acids content than do other conifers and all deciduous woods. In the United States, southern pines give higher yields with higher rosin acids content than do northern pines, although in Finland the reverse situation is true (21).

The saponification number of tall oils is always higher than the acid number, partly due to esters of fatty acids with sterols and other higher alcohols (about one-half of the sterols are esterified). Also, fatty acids containing hydroxy groups usually show an ester number due to lactones or estolides (esters of fatty acids with hydroxy groups of fatty acids). Even without hydroxy acids the unsaturated acids can form lactones and estolides by addition of a carboxyl group to a carbon-carbon double bond. Such additions are catalyzed

by concentrated sulphuric acid, as in the formation of γ - stearolactones from oleic acid or lactones of dihydroabietic acid. Many such complicated reactions may occur in the preparation and treatment of tall oil and these lead to further complications in the refining and conversion to derived products. Table 1 gives a representative picture of the composition and some of the characteristics of tall oil (1).

Manufacture and Purification of Tall Oil: The fine details involved in the manufacture and purification of tall oil are usually trade secrets. The first step is, of course, separation of the skimmings from the black liquor. When the latter has been partially concentrated in the vacuum evaporators, usually to about 22 per cent solids, it is lead into a tank proportioned for suitable retention time. Liquor outlet and an overflow launderer are arranged to permit the curdy "soap" to rise sufficiently to be scraped over the black liquor by a skimmer. This removal of skimmings has become an almost universal practice because it has a marked effect on improving the recovery of chemicals from the black liquor (7). Not all skimmings are made into tall oil at the mill. Some mills with smaller capacity either sell the skimmings to tall oil producers or burn them in the recovery furnace, depending on the market value. After as much black liquor as possible has settled out, a typical composition is: 30-35 per cent water, 5-10 per cent black liquor solids, the remainder being the soaps. This material has a fuel value of 8,000-9,000 B.T.U.

Table 1

Properties of Crude Tall Oil

Property	Min.	Max.
Density	0.95 g/cc	1.024 g/cc
Acid number	107	174
Saponification number	142	185
Iodine number	135	216
% Ash	0.40	4.62
% Moisture	0.39	7.20
Petroleum ether insolubles	0.1%	8.5%
Fatty Acids	18%	60%
Rosin Acids	28%	65%
Non-acidic bodies	5%	24%
Viscosity @ 18°C. (centipoises)	760	15x10 ⁶
Viscosity @ 100°C. (centistokes)	150	1200
Flash point (°F.)	350 and above	

per pound and a sodium content of about 6 per cent as Na_2O . Monographs have been prepared which correlate the value of the skimmings with the tall oil yields and the costs of salt cake and fuel (28).

The skimmings are acidified usually with sulphuric acid, although some European kraft mills are reported to use niter cake (sodium bisulphate). Sulphurous acid appears to remove some of the color and odor, therefore, its use might be justified. Operation may be batch or continuous. For the latter it is advantageous to have automatic pH control to avoid alkalinity, since this may lead to the formation of troublesome emulsions. These are difficult to break even on re-acidification. The cooking acid should not be too concentrated, for this may cause polymerization of some of the unsaturated compounds. It is common practice to use about four-normal acid. Lead may be used for parts which come in contact with the acid, although acid-proof brick is preferable. Separation of the liberated tall oil is facilitated by heat; therefore, the temperature is maintained near 100°C ., any excess of rosin acid above 35 per cent will crystallize and settle out. It, therefore, should be borne in mind that if the oil is to be pumped through pipes or stored in tanks, the temperature should be at least 25°C . In cases where it is desired to collect the rosin-acid crystals, it may be done so by sufficiently lowering the temperature and collecting the material which settles out. The rosin-acid crystals may then be purified by recrystallization from a suitable solvent

such as methyl alcohol. In this way, it is possible to obtain relatively pure rosin melting at (170-175° C.). These crystals may be fused and a clear, relatively light material will result, but unless stabilized by disproportionation, will recrystallize evolving heat and darkening in color (15).

Purification: Many methods have been suggested for the purification of tall oil and for the preparation of useful, derived products. C. J. West (30) lists 32 journal articles and 118 patents on purification out of 1,056 literature references on tall oil. The methods most frequently mentioned may be classified as follows (24):

1. Removal of color and odor:
 - (a) Treatment (usually in a solvent) with a mineral acid.
 - (b) Adsorption on an activated material such as carbon, decolorizing clay, or fuller's earth, the tall oil is usually the solvent.
2. Distillation under reduced pressure:
 - (a) Alone.
 - (b) With other gases: steam, inert gases, or solvent vapors.
3. Partition between immiscible solvents:
 - (a) After partial or complete esterification.
 - (b) After partial neutralization.
 - (c) Without prior treatment, using selective solvents.

One purification used with more or less modification by a number of refiners involves dissolving the crude tall oil in a neutral solvent, for example, naphtha, stirring with four-normal sulphuric acid at ordinary temperatures for about one hour. The acid used amounts to about 7 per cent by weight of the crude tall oil. The acidified sludge is then drawn off or centrifuged, washed with small portions of solvent,

and the washings are added to the tall oil solution. This is in turn washed with hot water (for example by reflux) until it becomes acid-free. The solution is then decolorized with bleaching clay or fuller's earth, filtered, and the solvent is distilled. A two-stage acid treatment, with 40 per cent of the acid used in the first stage, gives better color. Phytosterol may be recovered from the first-stage sludge (22).

Purification by acid treatment makes no essential change in the composition of the tall oil other than to remove some of the impurities, color, and odor. Subsequent crystallization may reduce the rosin acids content, but not below the point of saturation. Distillation of tall oil can yield fractions differing greatly from the crude material. Thus, one continuous vacuum distillation is reported to produce a fatty-acid fraction with no more than 2 per cent of rosin acids, low in saturated acids with equal quantities of oleic and linoleic acids and with no linolenic acid. This material is useful in the production of such compounds as non-yellowing alkyds, paste and liquid soaps, and emulsifying agents. The rosin-acid fraction of the tall oil distillate contains about 70 per cent rosin acids similar to those of wood rosin, and approximately 25 per cent fatty acids, mostly linoleic, of which about 20 per cent are conjugated. When esterified as in a maleic-pentaerythritol resin ester, these fatty acids form 25 per cent of an excellent drying oil which replaces a corresponding amount of oil in the final varnish. At elevated temperatures (530° F. or over) the fatty acids become

very corrosive and present handling problems (29).

Composition of Distilled Tall Oil: In addition to separation components, vacuum distillation produces changes in the chemical composition, since the tall oil is subjected to temperatures in the range of 250°-280° C. (depending on the pressure and other factors).

At these temperatures a series of chemical reactions take place. The phytosterols and other higher alcohols that have been free in the tall oil are esterified. Part of the sterol fraction may decompose. Some of the fatty acids are polymerized through the formation of six-member carbon rings by diene addition. The abietic type resin acids are further isomerized and disproportionated to dehydro-, dihydro-, and tetrahydroabietic acids, or may be dehydrogenated with the evolution of hydrogen gas. Part of the resin acids decompose to hydrocarbons and carbon dioxide or carbon monoxide and water. The carboxyl groups of another part of the resin acids are added to the double bonds of fatty acids or other resin acids to give estolides. Some resin acids may split off water to form acid anhydrides. The final result is that the distillation products of tall oil may contain small amounts of compounds not found in the starting materials (29).

With the exception of some separations of palmitic and the more volatile acids in the first fraction, the fatty acids of tall oil distillate have nearly the same composition as in the crude tall oil, i.e., they will normally consist of

almost equal parts of oleic and linoleic acids (including isomerized or conjugated linoleic acid) with usually less than 1 per cent linolenic acid. Small amounts of adipic ($\text{HOCO}(\text{CH}_2)_4\text{COOH}$), and sebacic ($\text{HOCO}(\text{CH}_2)_8\text{COOH}$) acids have been found in distilled tall oil. They are formed by the decomposition of oleic and other fatty acids. The author has been unable to find any data published on the composition of the resin acids in the fatty-acid fraction. It may be assumed that the dextropimaric type acids will be concentrated in the fatty-acid fraction since these resin acids are more volatile than the rest. The presence of these resin acids as lactones in the fatty-acid fraction may help to explain the difference between the saponification number and the acid number. Since most of the alcohols in crude tall oil are believed to be esterified during distillation, the unsaponifiable matter in the fatty-acid fraction must consist chiefly of hydrocarbons. The fatty-acid fraction of distilled tall oil contains no material insoluble in petroleum ether (29).

Eight resin acids, all which occur in tall oil, have been studied, five of which have the empirical formula $\text{C}_{20}\text{H}_{30}\text{O}_2$. These acids are of two types, the abietic type (abietic, neo-abietic, levopimaric, dehydro-, dihydro-, and tetrahydro-abietic acids) and the pimaric type (dextro- and isodextropimaric acids). The latter can be obtained from a mixture of resin acids by distillation; therefore, it seems probable that they would be concentrated among the resin acids in dis-

tilled tall oil fatty acids.

Hibbert and Phillips have stated the following: "The non-acidic bodies of tall oil consist mainly of alcohols and hydrocarbons. Only a few of these have been identified; the main component (70-90 per cent) appears to be β - sitosterol, $C_{29}H_{50}O$." A sterol with rotation $[\alpha]_D^{25} +24.8^\circ$ has been reported also. The latter appears in greater abundance in the "tall oil pitch." Therefore, it is thought to be formed by hydrogenation of β - sitosterol during the distillation process. Small amounts of lignoceryl alcohol ($C_{24}H_{49}OH$) have been found also. Hibbert and Phillips have postulated that this material is identical with the "wax" reported in the unsaponifiable fraction of the ether extract from jack pine (15).

Tall Oil Pitch: When crude tall oil is distilled under reduced pressure, a residue with variable composition remains, this material is known as tall oil pitch. It is formed in yield between 25 and 30 per cent depending on distillation conditions. Tall oil pitch has a high content of esters, unsaponifiables, and petroleum ether insoluble materials. Most tall oil pitches contain about 1.5 per cent methoxyl; this is an indication of the presence of wood phenols or lignin. Analytical results indicate that in tall oil pitch simple rosin acids are combined with each other or with simple fatty acids to form difficult saponifiable acid esters, which in the standard separation scheme, appear as fatty acids or rosin acids, depending on whether the free carboxyl group

belongs to a fatty acid or a rosin acid. This problem is further complicated by the methoxyl containing components which appear in both the rosin and fatty-acid fractions and the saponifiable neutral components (probably lactones, esters or anhydrides).

Tall oil pitch has been used extensively as a sizing agent for kraft paper and wall board, whereby 1.6 parts of tall oil pitch replaces one part of regular rosin size (10).

Present-Day Uses of Tall Oil: Perhaps the use of tall oil, which is of greatest interest here, is that it is an abundant source of rosin; the paper industry is probably the largest consumer of rosin, since a very large majority of the papers made contain rosin as a sizing agent. Other important uses of tall oil include the preparation of adhesives, asphalt emulsions, binders, coil oils, detergents, driers, drying oils, varnishes and wetting agents. One of the most important and rapidly growing uses of tall oil is in the preparation of esters for use in drying oils. Others are additives for lubricants (extreme-pressure greases and cutting oils), hydraulic fluids; surfactants (such as wetting agent), plasticizers, and resins. Also, together with phthalic or maleic acids and polyhydric alcohols, especially pentaerythritols, tall oil esters form alkyd resins of superior weather-resistant properties (4, 26).

Economic Aspects: Although commercially available in

Europe shortly after the turn of the century, it wasn't until the 1930's that tall oil was extensively produced in the United States. The following data will give a rough idea of the tall oil production from 1950 to 1953. (in tons).

<u>Year</u>	<u>Crude</u>	<u>Refined</u>
1950	154,901	56,007
1951	199,118	67,290
1952	156,385	53,930
1953	159,226	59,383

Throughout 1952 and 1953, crude tall oil sold between \$40 and \$45 per ton; and the refined or distilled tall oil sold between \$100 and \$150 per ton, depending on its quality.

Recent and continuing expansion in the alkaline pulping process of resinous woods, especially in the southern United States, has raised the potential production of tall oil enormously. The tall oil industry is not subject to any seasonal fluctuations (29).

SURVEY ON CATALYSIS

History of Catalysis (24) It was probably about the middle of the eighteenth century when catalysts, as we know them today, were first used in the synthesis of chemical compounds. The first well-known process in which catalysts were used was in the chamber process for the preparation of sulphuric acid. Here, sulphur dioxide was oxidized to sulphur trioxide in the presence of small amounts of nitrogen oxides. These nitrogen oxides acted as a catalyst. Another contribution to this field of science was brought about by Parmentier in 1781 when he developed a method for the saccharification of starches using acids as catalysts. Until the discovery by Lavoisier of the chemical nature of combustion and of the composition of water at the end of the eighteenth century and the annunciation of Dalton's atomic theory, a basis for the interpretation of catalytic phenomena was non-existent. However, during the nineteenth century, catalytic phenomena attracted much interest by such scientists as Berzelius, Mitscherlich, and Faraday.

Ostwald, in 1901, defined a catalyst as any substance which alters the velocity of a chemical reaction without appearing in the end product and predicted that catalysis will have a wide-spread industrial application. Then Sabatier

and Ipatieff began their pioneering researches in catalysis, thus, opening up a field of chemistry and engineering which has enormous industrial consequences.

Catalytic Theory: Although the nature of the phenomena associated with catalysis is only partly understood; it has been useful to view the factual results in the light of chemistry, physics, and mathematics. There is still a considerable way to go before reaction kinetics can be interpreted from a catalytic point of view, the major reason being that knowledge of the influence of impurities and the reaction products on the reaction mechanisms is still deficient (24).

In 1922 Bronsted assumed that catalytic reactions, and possibly all reactions, proceed by the formation of a "critical complex," which decomposes into substances resulting from the reaction:



where A and B are the reactants, X the critical complex, and C and D the reaction products. The formation of the critical complex is slow and governs the velocity of the reaction. The rate of formation of X is determined by the activities of A and B (24).

In heterogeneous catalytic reactions, which are of main interest here, the catalyst and the reacting and resulting substances are in different phases. Heterogeneous reactions take place on a phase boundary. It has been shown that action of a heterogeneous catalyst is due to:

1. residual surfaces (van der Waals forces; chiefly contributing to physical adsorption);
2. molecular forces (contributed by the liquids);
3. metallic lattices (unsaturated lattice forces);
4. homopolar forces in atomic lattices;
5. electrostatic forces in ionic lattices (31).

The type and rate of reaction taking place on a contact surface will essentially depend on:

1. the nature of the unsaturated forces on the surface of the catalyst;
2. the nature of the reactive forces on the reacting substances and of the solvent if such is used;
3. the adsorption, spatial arrangement, deformation, and perhaps, isomerization of the reactants on the contact surface;
4. the free energy decrease and the heat of formation in the chemical reaction taking place on the surface of the catalyst;
5. the time of contact of the reaction products;
6. the temperature and pressure (in a gas process);
7. side reactions (31).

Catalytic Hydrogenation: Catalytic hydrogenation is the chemical addition of hydrogen to compounds in the presence of a suitable catalyst. This process enables one to eliminate carbon, nitrogen, sulphur, and halogens from a chemical compound. The substance to be hydrogenated is brought in contact with a finely divided metal or metal oxide which functions as a catalyst. The material to be hydrogenated (usually in solution) plus the catalyst (generally dispersed in the

solution) is subjected to an atmosphere of elemental hydrogen (usually at elevated temperature and pressure).

A good catalyst for catalytic hydrogenation must fulfill the following requirements:

1. be stable in the presence of the reactants
2. adsorb and activate the hydrogen acceptor
3. adsorb and activate the hydrogen
4. hold the activated hydrogen and hydrogen acceptor in the proper relationship for reaction to occur
5. desorb or set free the reaction product(s)

The rate of hydrogenation is a function of the following:

1. the acceptor of the hydrogen (the unsaturated compound)
2. the quality and quantity of the impurities in solution
3. the temperature during hydrogenation
4. the pressure of hydrogen above the solution
5. the quality and quantity of the solvent
6. the quality and quantity of the catalyst present
7. the ratio of catalyst to hydrogen acceptor
8. the thoroughness of mixing of the hydrogen, catalyst and the hydrogen acceptor
9. the solubility of hydrogen in the media
10. the activity of the catalyst
11. the temperatures involved in all stages of the hydrogenation experiment
12. time

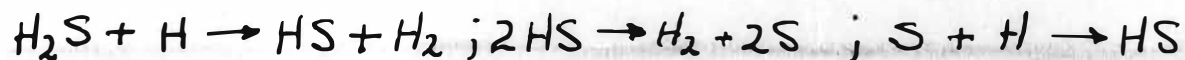
Catalyst Poisons: In the work to be undertaken, the problem of catalyst poisoning is of utmost concern. Tall oil

contains numerous materials which render hydrogenation catalysts inactive. The literature contains many articles pertaining to the theory and remedies of catalyst poisoning. There appears to be a wide variety of theories regarding this subject, all of which may be somewhat true; although, all of the investigators seem to agree on a single method of eliminating this problem.

It has been proposed by Thomas Andrews (16) that the materials generally found in oils which have a poisoning effect on hydrogenation catalysts are nitrogenous material or unsaponifiable matter. He also proposed that this is more a physical phenomenon than a chemical one.

Treidlin and Ziminova (17) have hypothesized a theory on catalyst poisoning which seems to be a representative summation of many of the other proposed theories. They theorized that poisoning is due to adsorptive "blocking" of the active centers, but it is due to the removal of dissolved atomic hydrogen, which is an essential promoter of the catalyst. Some of the materials which are poison to such catalysts as Pd, Pt, Ni, and Co are O, S, Se, Te, P, As, Sb, Bi, Cl₂, Br₂, I₂, and many more. The poisoning cannot be due to a reaction with the metal, especially as I₂, which doesn't react with any of the Pt-group metals at all, but is a poison to catalysts even at room temperature. In all cases, the poisoning consists simply of a "depromotion" through the removal of atomic hydrogen. Hydrogen sulphide is a strong catalyst poison; this can be ex-

plained as follows:



Thus, such a material takes atomic hydrogen from the active surfaces and converts it to molecular hydrogen which is gaseous and can leave the solution.

Removal of Catalysis Poisons: Russell Vivian and Hasselstrom (5, 6) have developed a method for the pretreatment of tall oil before hydrogenation by heating in the presence of a disproportionation catalyst renders the tall oil less difficult to hydrogenate and increases the stability of the hydrogenated products. The pretreatment is carried out by heating the tall oil to temperatures in the range of 100-240° C. from one-fourth to six hours with agitation and preferably in an inert atmosphere of carbon dioxide, nitrogen, or hydrogen. Two to three per cent of a disproportionation catalyst such as bleaching clay, bleaching carbon, or spent hydrogenation catalyst should be present. The treated tall oil is then separated from the disproportionation catalyst by filtration or other means.

SURVEY ON TALL OIL HYDROGENATION

The objective of hydrogenating tall oil is to chemically add hydrogen to the carbon-carbon double bonds found in many of the unsaturated fatty acids present in the oil. There are often minute quantities of unsaturated aliphatic compounds other than fatty acids which stand an equal chance of becoming saturated by hydrogenation. The unsaturated aliphatic compounds present are always hydrogenated, preferentially to the unsaturated, aromatic compounds present such as the resin acids (2).

The effect of hydrogenating the fatty fraction of the tall oil is that the melting point of the oil is increased. Thus, at room temperature, the hydrogenated tall oil is more solid (less oily). It also is a general rule that a hydrogenated oil such as tall oil is lighter in color than before hydrogenation (2).

The literature contains many articles pertaining to the hydrogenation of tall oil, most of which have a common objective, although the problem is approached in a variety of ways. With the facilities available, the writer was only able to obtain abstract material pertaining to this subject, this is mainly due to the fact that specific information regarding such processes are usually trade secrets.

The general method of approach is as follows: since the tall oil is rather viscous, it is best to put it in a solvent solution so that more effective agitation and catalyst dispersion may be achieved. A given quantity of Raney nickel catalyst are added to the solution. The solution is then placed in a hydrogenator bomb, and the air above the solution is replaced with hydrogen at an elevated pressure. Generally the temperature is elevated various degrees. Hydrogenation then proceeds for given lengths of time.

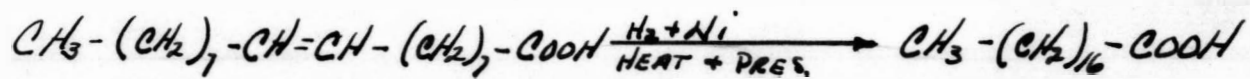
Some of the proposed methods of tall oil hydrogenation are as follows: the tall oil (either crude or refined) is pretreated with activated carbon, fuller's earth, bleaching clay, etc. to remove potential catalyst poisons (5, 6). The pretreated tall oil is then put in solution (50 per cent by weight) using 1,4 - dioxane (2) or 95 per cent ethyl alcohol (5) as solvents. Raney nickel is then added, ranging from 3 to 33 per cent, based on the weight of tall oil. The hydrogenator bomb now containing the pretreated tall oil in solution plus the catalyst is subjected to pressures of hydrogen ranging from 50 to 1,500 psi., temperatures ranging from 100 to 350° C., and reaction times varying from $\frac{1}{2}$ to 16 hours, generally depending on the hydrogenating conditions and the degree of hydrogenation desired (2, 3, 5, 6, 8, 9, 11). The writer chose the above method for presenting this data because there appeared to be no pressure-temperature time correlation. Had there been more specific information available,

probably some conclusions could have been arrived at.

The literature cited another rather interesting process in which an aqueous solution of tall oil soaps was hydrogenated by subjecting the solution to about 50 psi. of hydrogen at temperatures ranging from 40 to 200° C. in the presence of Raney nickel. This produced a light-colored material which was suitable for the soap industry (27).

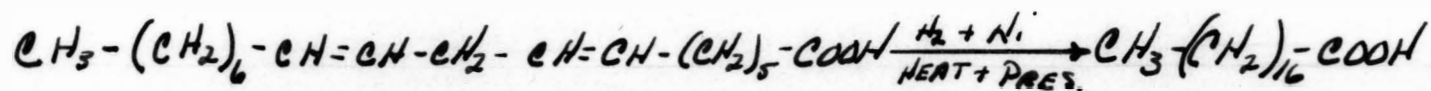
Thomas Steadman (20) proposed a method for increasing the rate of hydrogenation of fatty acids by adding minute quantities of surface-active materials. He claims that by adding approximately 0.3 per cent of a wetting agent such as sodium lauryl sulphate to the material to be hydrogenated, the reaction time was greatly reduced.

The major portion of the hydrogenation occurs at the carbon-carbon double bonds of the unsaturated fatty acids. The reactions are on the following page.



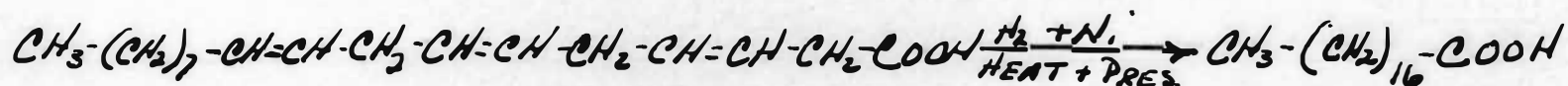
OLEIC ACID

STERIC ACID



LINOLEIC ACID

STERIC ACID



LENOLENIC ACID

STERIC ACID

HYDROGENATION REACTIONS FOR THE THREE MAJOR FATTY ACIDS
IN TALL OIL

CONCLUSION

It should now be realized that tall oil, with such a variable composition, will be very difficult to hydrogenate. The problem of catalyst poisoning is of utmost concern.

The literature cited on tall oil hydrogenation contains a wide variety of proposed methods on carrying out this reaction. Due to the limitations of our hydrogenating facilities, the hydrogenation will be carried out under relatively mild conditions *i.e.*, low temperature and pressure.

Due to limited facilities and specific information regarding tall oil hydrogenation, much of the work will have to be done by trial and error.

According to the literature, hydrogenated tall oil has the following properties which make it more suitable for paper sizing than non-hydrogenated tall oil: whiter, more solid (less oily) and less polar, which will yield better water repellency to paper.

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PROPOSED EXPERIMENTAL OUTLINE

PROPOSED EXPERIMENTAL OUTLINE

Purpose: The primary objective of this experimental work is to prepare a material from tall oil which will be more suitable for sizing various low grades of kraft paper.

It is hoped that hydrogenation will change the properties of tall oil in such a way that the resultant material will lend itself more effective as a sizing agent.

If the hydrogenation of tall oil is successfully attained, a size will be prepared and incorporated in hand-sheets so as to point out the relative sizing efficiency of this material and its effect on the brightness and paper strength.

General Discussion: It is felt that tall oil with such a variable composition will be very difficult to hydrogenate. Probably the major source of trouble will relate to catalyst poisoning. It, therefore, will be of utmost concern to investigate means of removing materials from the tall oil which will yield hydrogenation catalysts inactive. Even with most of the catalyst poisons removed, hydrogenation will probably proceed very slowly; and the extent to which the tall oil will hydrogenate may be limited by the hydrogenation facilities available.

If tall oil hydrogenation is attained, it is anticipated that the major improvement brought about by hydrogenation will be the lighter color i.e., the rate of brightness degradation of paper will be decreased. Little or no increase in the sizing efficiency of hydrogenated tall oil size is anticipated, nor is hydrogenation expected to greatly affect the rate of strength degradation of the tall oil sized paper.

Materials: Listed below are the materials which will be used in this experimental investigation:

1. Tall oil (Southern Pine)
2. Tall oil soap skimmings (from third effect evaporator)
3. Raney nickel alloy (hydrogenation catalyst)
4. Hydrogen gas (bottled)
5. A bleached sulfite pulp (for sizing study)
6. Hercules rosin (70% fortified)
7. Alum
8. Activated carbon
9. Several organic solvents
10. Inorganic reagents for iodine value determination

Hydrogenation will be attempted using Raney nickel as the only catalyst; several organic solvents will be used as solvents for the tall oil. Hydrogenation of the tall oil soap skimmings will be attempted using water as the solvent.

General Procedure: The tall oil will be put in solution, either aqueous or solvent depending on the sample. The resultant solution will be treated with activated carbon to remove potential catalyst poisons. Upon removal of the activated carbon, the sample will be ready for hydrogenation. If hydrogenation is successful, a size will be prepared from the hydrogenated tall oil. Handsheets are to be formed using the hydrogenated tall oil size as the sizing agent, and the properties of the handsheets are to be tested and compared.

Specific Procedure: Since the literature revealed no specific information regarding tall oil hydrogenation, some of the experimental procedure proposed at this time will probably have to be changed or modified when the laboratory investigation is actually carried out.

The proposed procedure is as follows:

1. Preparation of tall oil solutions

The objective here is to prepare a tall oil solution using a single solvent which is suitable for the hydrogenator available. Solutions of tall oil or tall oil soap skimmings should be prepared at concentrations such that the viscosity of the solution at room temperature will be approximately that of water. In preparing tall oil solutions, the choice of solvents will be limited to toluene and dioxane. Both of these should be sufficiently miscible with tall oil

to form a homogenous solution at room temperature. An aqueous solution of tall oil soap skimmings will be prepared in a similar manner. A small amount of heat may be used to increase the rate of solution.

2. Removal of potential catalyst poisons

Material present in tall oil which adsorb on hydrogenation catalysts, thus yielding them inactive, will also adsorb an activated carbon. Therefore, if the tall oil solution is treated with activated carbon before it comes in contact with the catalyst, most of the catalyst poisons will be removed. It is, therefore, the objective of this step to remove these catalyst poisons with an inexpensive material before they have a chance to spoil an expensive catalyst. This step is very important since the hydrogenation reaction will be nil if the hydrogenation catalyst is inactive.

It is proposed that activated carbon be added to the tall oil solutions to the extent of 5% based on the weight of tall oil solids. The solution is to be heated to not more than 100°C. and shaken occasionally for about one-half hour. The activated carbon will then be removed by passing the solution through a fluted filter paper. The tall oil solution, now assumed free from catalyst poisons, is ready for hydrogenation. The exact concentrations of the solutions will be determined following separation of the activated carbon by evaporation of solvent at 110°C. This will enable

one to know the exact quantity of tall oil entering the hydrogenator. The same procedure is to be carried out on the aqueous solution as well as the solvent solutions.

3. Activation of Raney nickel catalyst

The Raney nickel catalyst was activated as prescribed in the J. Am. Chem. Soc., 54, 4116-7, (1932).

4. Hydrogenation of tall oil

The objective here is to chemically add hydrogen to the double bonds of the unsaturated fatty acids present in the tall oil. In the case of the aqueous solution, the salts of the fatty acids are to be saturated. The hydrogenation is to be carried out in a Parr Bomb Hydrogenator made available by the Chemistry Department at Western Michigan University. A known quantity of tall oil in solution is added to the hydrogenator along with an appropriate amount of Raney nickel catalyst. The hydrogenation pressure in the reaction bottle is to be raised to maximum (60 psi) and the shaker started. With the aid of the pressure gage on the hydrogenator, it will be possible to determine whether or not the reaction is proceeding; a decrease in pressure indicates a consumption of hydrogen by the sample. If the reaction does not proceed under these conditions, a heating element will be installed on the reaction bottle of the hydrogenator. If the pressure in the reaction bottle does not decrease noticeably after several hours, a different solution should be tried.

5. Removal of spent catalyst from hydrogenated samples

Since the Raney nickel catalyst is so finely divided, it probably would not be completely separated by filtration; therefore, it is proposed that this separation be carried out by centrifuging and decanting the supernatant liquid, which is the hydrogenated tall oil solution.

6. Removal of solvent

In the cases of the solutions with organic solvents, the solvents must be removed so that the hydrogenated oil can be saponified and put in an aqueous media. It is proposed that the solvents be stripped by putting the solutions in evaporating dishes in a desiccator under reduced pressure, thus increasing the rate of evaporation of the solvents. Aside from preparing sizing agents from the residues, the iodine numbers are to be determined on these solvent-free samples. In the case of the aqueous tall oil soap solution, the water is to be evaporated by a means similar to the one described above. Here the only purpose is to obtain a solvent-free sample for iodine number determinations. After determining the final concentration of the soap solution, this material is ready to be used as a sizing agent.

7. Determination of iodine numbers

Since the iodine number is an index to the degree of saturation of fatty materials, it is desirable here to know the change in iodine number of the tall oil which was brought about by hydrogenation. Since from the previous step solvent-

free tall oil or tall oil soap samples are available, the iodine numbers of the hydrogenated and non-hydrogenated materials are to be determined. The procedure to be used for determination of iodine numbers comes from Biochemistry Laboratory Methods, Marrow, John, Wiley & Sons, Inc., New York, 1927.

8. Saponification of the tall oil

The objective here is to react tall oil with sodium hydroxide, thus converting the rosin and fatty acids to sodium salts of these acids which are precipitable with acid or alum. The proposed procedure is as follows: obtain a small tall oil sample of known weight, add a known small quantity of water, titrate with N/10 sodium hydroxide to a thymol blue end point or to a point where the tall oil is completely soluble in the aqueous media at room temperature.

9. Preparation of sizing agent

The saponified aqueous samples will be considered sizing agents after the concentrations are accurately determined. The concentrations are to be determined by evaporating the water from known weights of the aqueous solutions in a drying oven at 110°C; knowing the weight of the residue, the concentration is easily obtained. For the sizing study to be carried out here, the samples will be diluted to 1.00% solids.

10. Preparation of handsheets

The objective here is to prepare handsheets into which the prepared tall oil sizing agents will be incorporated.

Tappi Standard Handsheets are to be formed according to T205-M58 using a sulfite pulp with a relatively high freeness so that the properties of the size will be more apparent. A set of handsheets will be sized with a commercial rosin size so as to be a standard. It is proposed that the handsheets will be sized as follows:

- a. Control
- b. 1.5%, 3.0%, 5.0% hydrogenated size based on weight of fiber.
- c. 1.5%, 3.0%, and 5.0% non-hydrogenated size
- d. 1.5%, 3.0%, and 5.0% commercial rosin size

Three sheets of each type are to be formed. The sizing agents are to be flocculated with alum to a pH of 5.0.

11. Testing of the handsheets

The sized handsheets are to be tested for brightness, strength, and sizing. From the results of these tests, certain conclusions regarding the properties of the sizing agents will be deduced. It is proposed that the brightness determinations be run on a GE brightness tester. Mullen Tests will suffice as an index to strength and the sizing will be tested on a Currier Size Tester.

The above discussion has only covered the line of approach which seems most direct. There are, however, other considerations which indicate that other angles of attack would be of value.

THE EXPERIMENTAL INVESTIGATION

THE EXPERIMENTAL INVESTIGATION

The course of this experimental investigation into the possibilities of preparing an effective sizing agent from tall oil by hydrogenation generally followed the procedure as detailed in the previous section, "Proposed Experimental Outline." Small modifications were made when the actual work indicated more suitable methods.

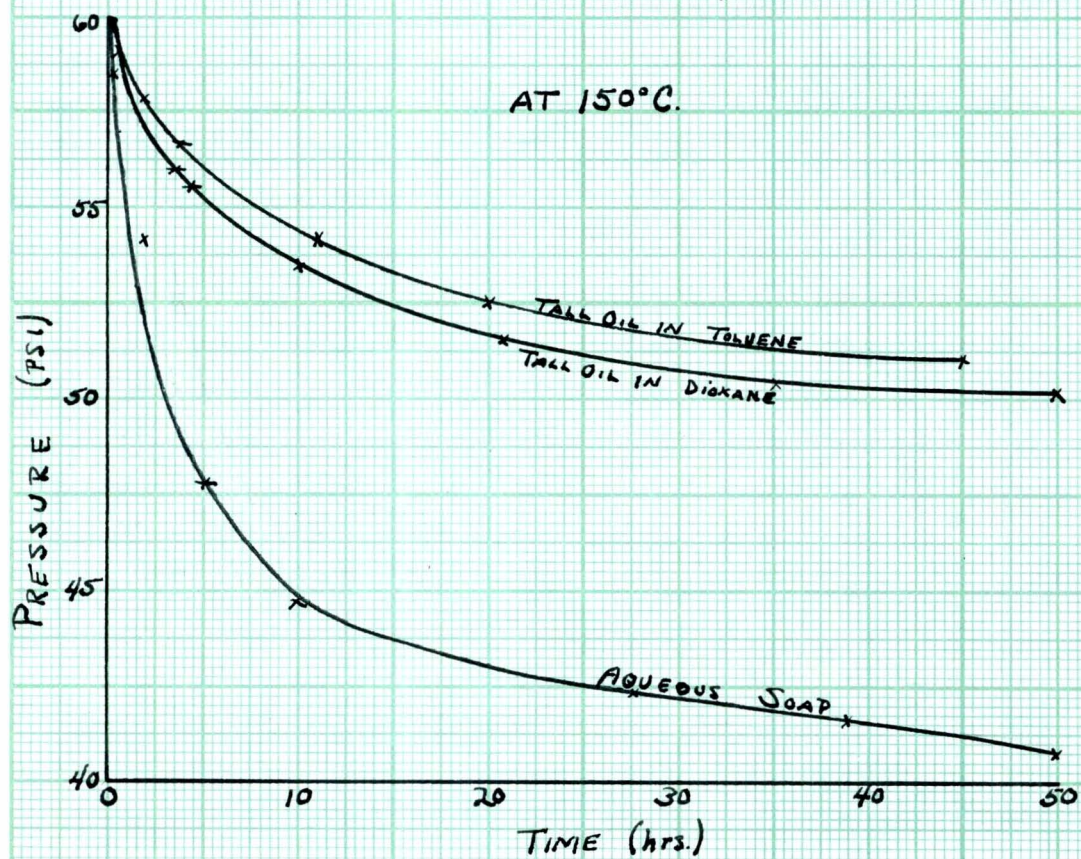
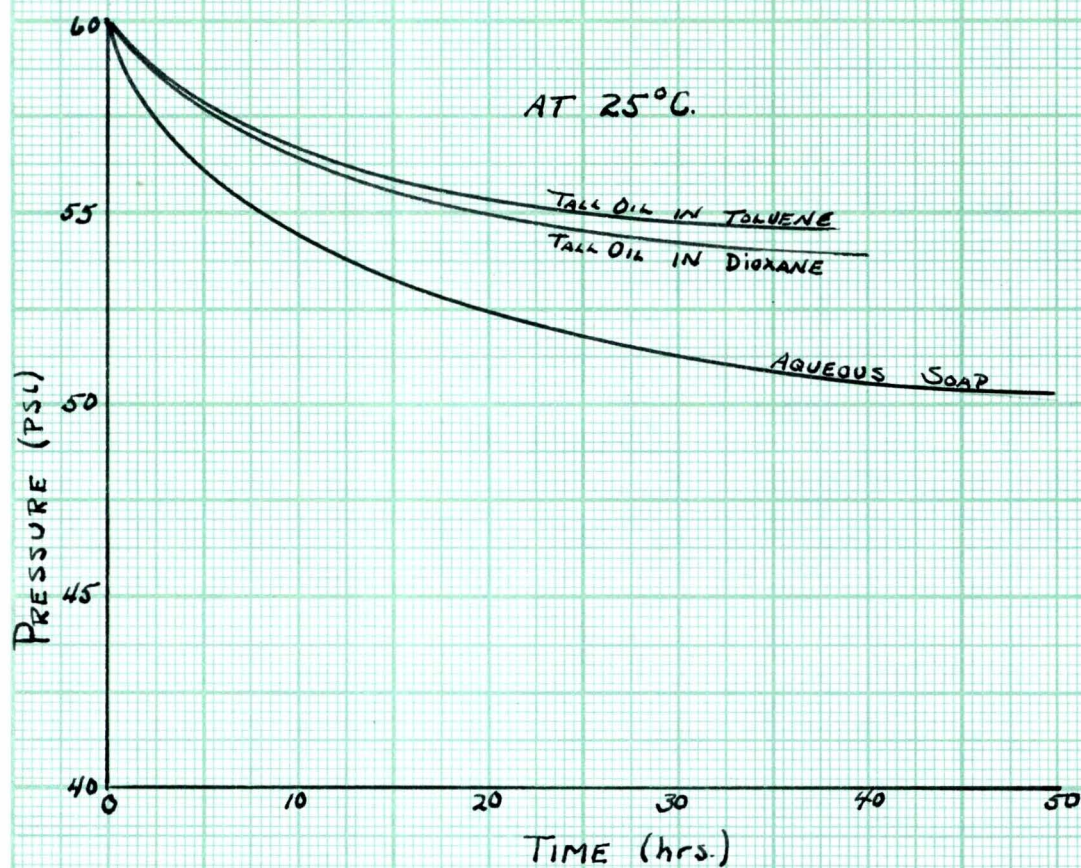
Basic Experimental Procedure: The procedure which was actually utilized can best be discussed by noting the modifications and extensions which have been made in the tentative outline. Items which were left rather vague in the tentative outline will be pinpointed here.

The tall oil and tall oil soap solutions were prepared and the catalyst poisons removed. The solvents which were actually used are toluene, dioxane, and water. The solutions which were to be hydrogenated were made up to a concentration of 15% solids; this seemed to be the maximum concentration at which the viscosity was suitable for the hydrogenating apparatus at room temperature. Four hundred ml. of the 15% solutions were to be hydrogenated at room temperature and 60 psi. Under these conditions, hydrogenation proceeded very slowly; after 50 hours of reaction

this was

time there was only about a 5 psi pressure drop in the hydrogen resevoir tank with the samples in organic solvents and a slightly greater pressure drop in the case of the aqueous soap sample. This small degree of hydrogenation brought about no apparent change in the properties of the tall oil or tall oil soap solutions. In order to bring about further hydrogenation, the reaction bottle was wrapped with 50 feet of resistance wire and covered with asbestos so that when a voltage was applied across the ends of the resistance wire, the reaction bottle was heated. It was found from a voltage-temperature relation that at 60 volts the temperature in the reaction bottle was $150^{\circ}\text{C}.$, which seemed to be a good temperature for hydrogenation under the conditions. Hydrogenation of new samples was attempted under the new conditions. The addition of heat to the reaction mixture had little or no affect on the degree of hydrogenation of the samples in organic solvents, while the tall oil soap in the aqueous solvent was hydrogenated sufficiently under these conditions to cause the reaction mixture to behave as an off-white gel structure. To confirm the remarkable results obtained by hydrogenating the 15% aqueous solution of tall oil soaps at 60 psi and $150^{\circ}\text{C}.$, the reaction was duplicated. The same results were obtained. There was a pressure drop of nearly 20 psi over a 50-hour period. From the pressure-time relations on the following page, it can be seen how the rates

RATES OF HYDROGENATION



and relative degrees of hydrogenation are affected by temperature and nature of the solvent. Here it is assumed that the fatty fraction of the tall oil soap is sufficiently changed by hydrogenation to warrant its study as a sizing agent. The gel structure obtained by hydrogenating the soaps was broken by adding an equal volume of water with vigorous agitation until a homogeneous solution was obtained. The spent catalyst was removed by centrifuging and the supernatant liquid collected.

Although until now it was assumed that hydrogenation of the fatty fraction of the tall oil soap brought about the change, it is the purpose of this step to prove that the fatty fraction was hydrogenated. Samples of hydrogenated and non-hydrogenated aqueous soaps were put in evaporating dishes in a desiccator under reduced pressure. It was felt that raising the temperature of these samples may tend to change the chemical composition so the evaporation of the aqueous media was carried out at room temperature. Nearly a week's time was required to evaporate these samples to dryness. Iodine values were run on both the hydrogenated and non-hydrogenated samples according to the procedure in Marrow's Biochemistry Laboratory Methods, John Wiley & Sons, Inc., New York, 1927. Three trials on both samples showed that hydrogenation changed the iodine value from 254 for the non-hydrogenated soap to 195 for the hydrogenated soap. This

was sufficient proof that hydrogenation brought about the obvious change in the tall oil soap.

Sizing agents were prepared from both the hydrogenated and non-hydrogenated soap solutions, and handsheets were prepared as indicated in the proposed outline.

The sized handsheets were tested for brightness on a GE brightness meter, sizing by ink floatation, and strength by tensile tests.

The correlation and discussion of these results follow.

DATA

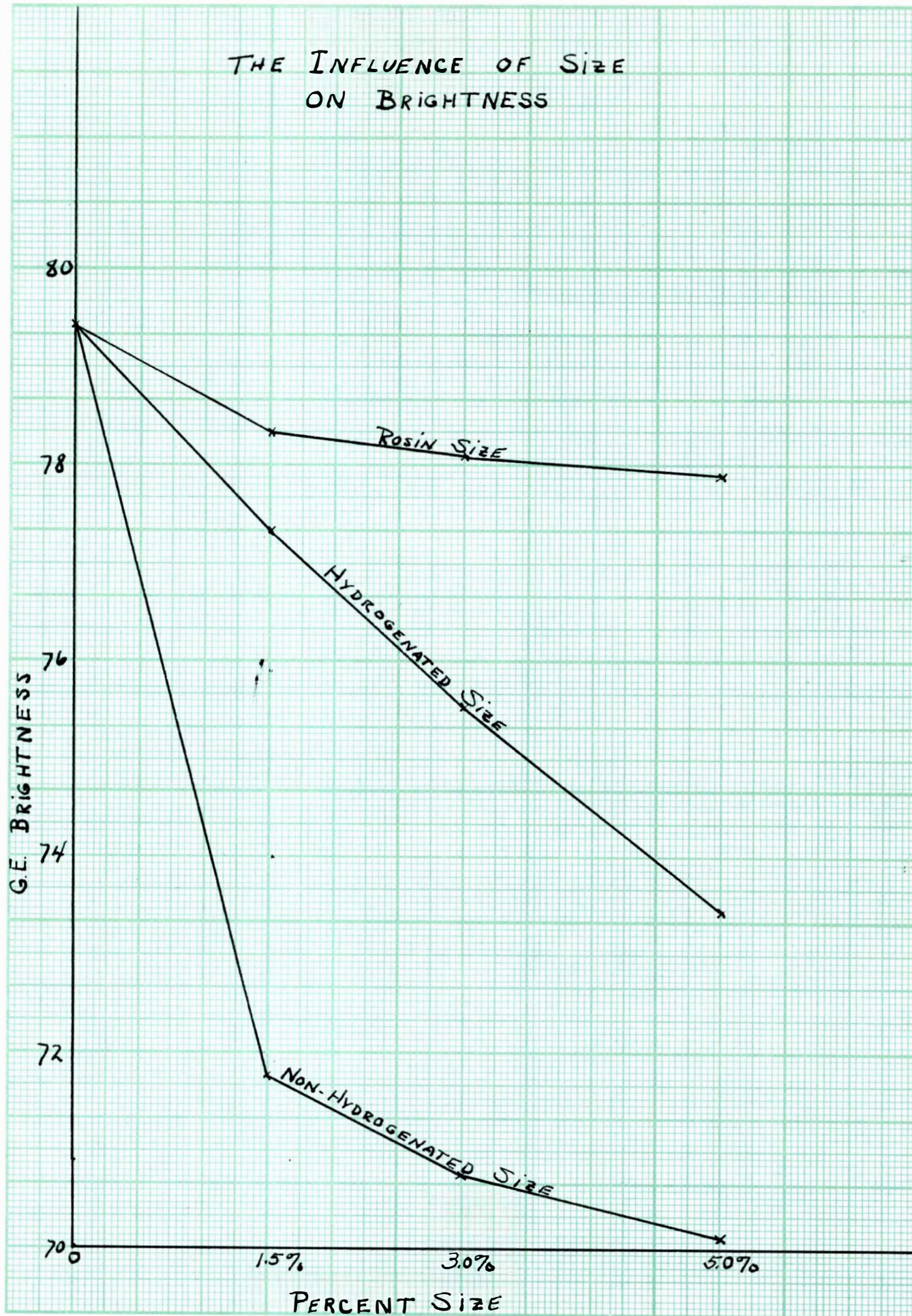
		Brightness (10 tests)	Tensile (6 tests)	Ink Floatation (3 tests)
Control		79.4	3.22 #	0 sec.
Hydrogenated Size	1.5%	77.3	2.77	4.7
	3.0%	75.6	2.62	642
	5.0%	73.6	2.43	769
Non-hydro- genated Size	1.5%	71.8	2.80	5.0
	3.0%	70.7	2.67	613
	5.0%	70.1	2.40	801
Rosin Size	1.5%	78.3	2.73	5.0
	3.0%	78.1	2.81	1012
	5.0%	77.9	2.40	∞

Experimental Observations: The aqueous solution of tall oil soap was the only solution which was successfully hydrogenated. In the cases of the tall oil in organic solvent solutions, there was no apparent change brought about by the relatively small pressure drop, as can be seen from page 41. Further discussion concerning the tall oil in organic solvent solutions will be omitted. The aqueous soap solution was converted from a dark-brown solution with a viscosity at 15% solids like that of water to an off-white or tan-colored material which behaved as a gel. The hydrogenated product also had the property of being more opaque than the starting material. Even after dilution to 1.00% solids, the hydrogenated sample was much more viscous than the non-hydrogenated sample.

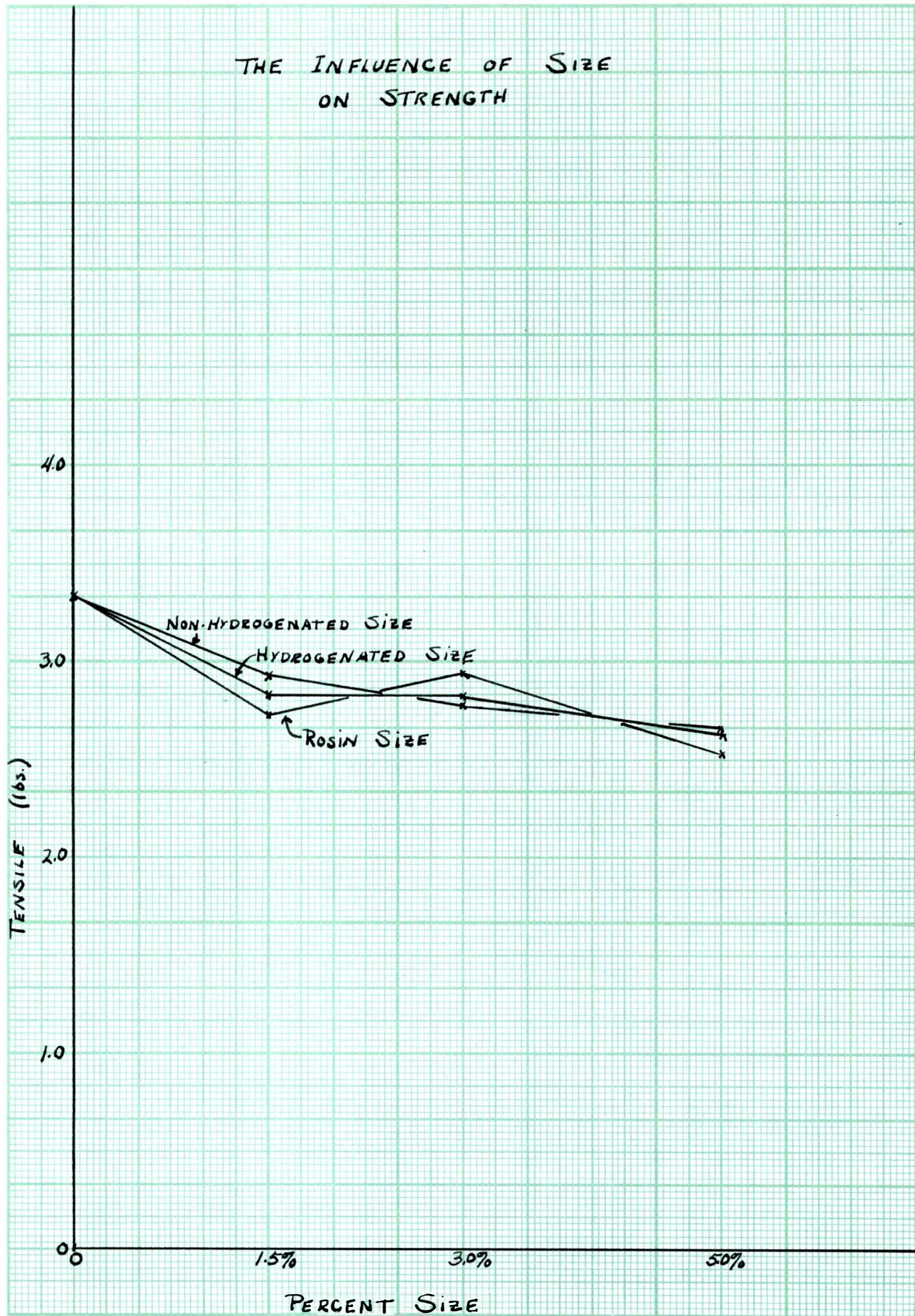
As indicated by the iodine numbers of the hydrogenated and non-hydrogenated samples (254 and 195 respectively), a satisfactory degree of saturation was attained, although the hydrogenation carried out here was far from complete.

From the graphs which follow, it can be seen how the tall oil sizes affect the brightness, strength, and water repellency of paper.

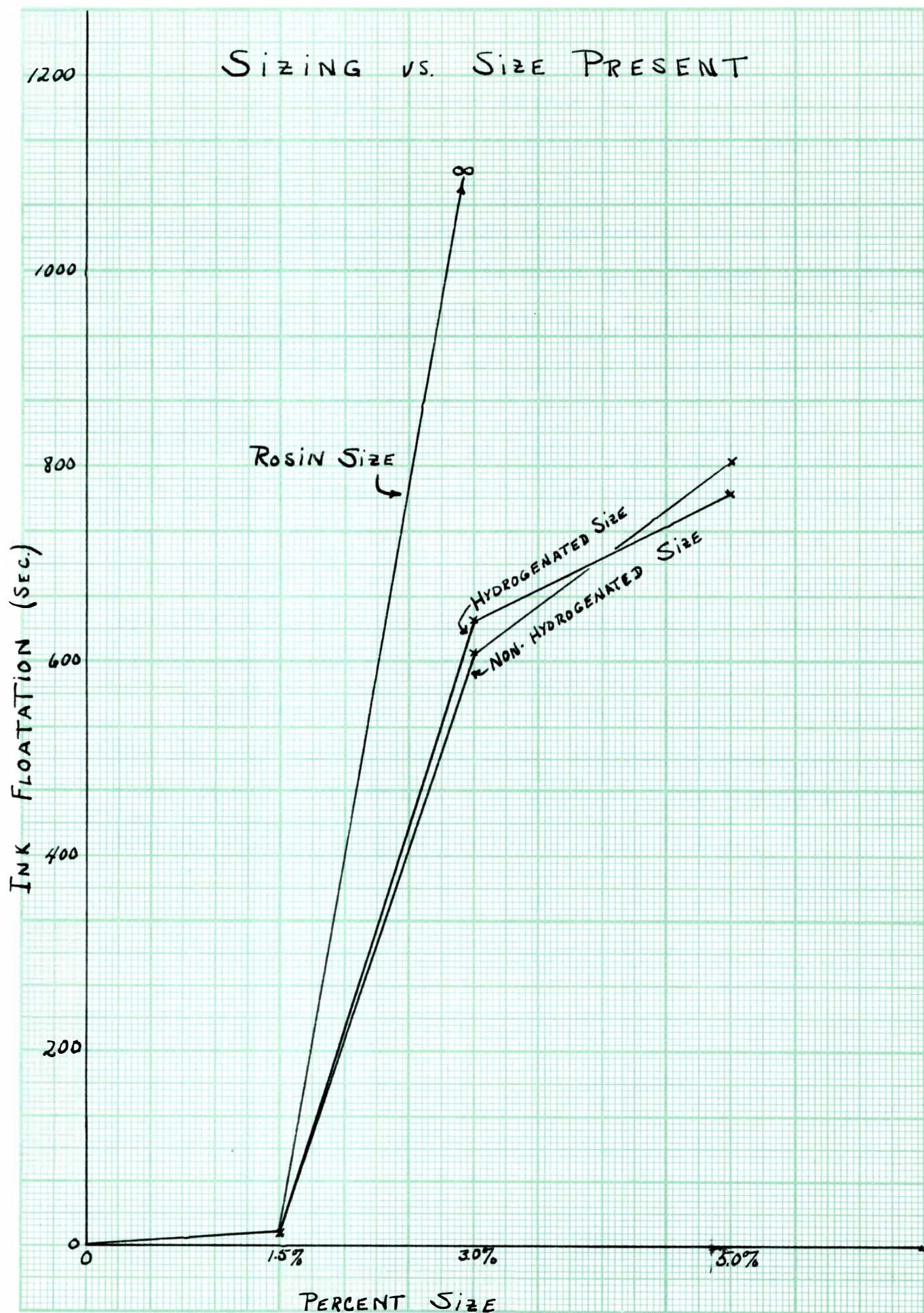
THE INFLUENCE OF SIZE ON BRIGHTNESS



THE INFLUENCE OF SIZE ON STRENGTH



SIZING VS. SIZE PRESENT



As seen from the figure on page 46, the hydrogenated tall oil size decreases the brightness of paper slower with sizing than does non-hydrogenated tall oil size, although this material does not compare to commercial rosin size.

Since the sizing study is based on the amount of size added rather than the amount retained, specific deductions should be omitted.

From the figure on page 47, we can see the general trend i.e., paper strength or hydrogen bonding is reduced as a result of sizing. This is a well-known fact. Since the tensile test results lie in a very narrow range and this study was not carried out on a statistical basis, no specific deductions can be made regarding the relative rates of strength degradation of the three sizes used.

From the graph on page 48, it can be readily seen that the tall oil sizes prepared do not compare to commercial rosin size. It appears that hydrogenation did little or nothing to the sizing efficiency of tall oil size.

Conclusions: This investigation was conducted with the intent of preparing a material from tall oil which could be utilized as a sizing agent for certain low grades of paper. It was proposed that by hydrogenating such a material, a product would be obtained which would lend itself more effective as a sizing agent i.e., whiter and less oily (more waxy).

From the course and methods of this work, the following conclusions are apparent:

1. By sufficiently hydrogenating tall oil soap, a material is obtainable which does not destroy the brightness of paper as rapidly with sizing as does non-treated tall oil soap.
2. Hydrogenation of tall oil soap does not bring about any great change in the ability of this material to preserve the strength of the resultant sized papers.
3. From the results of the sizing study, the sizing efficiency of tall oil soap is not noticeably changed by hydrogenation of the starting material.

From the results of this investigation, it is apparent that by hydrogenation of tall oil a material is obtainable which is more suitable for sizing paper in that more size can be added before the brightness of the sized paper is dangerously diminished.