May 21st, 1943

Report No. P-2070

NAVY DEPARTMENT

FR-2070

REPORT ON

A Summary of a Literature and Patent Search on Synthetic Drying Oils

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D. C.

Number of Pages: Text - 29

Authorization: As a part of Bureau of Aeronautics P. O. 112/43 dated 13 June 1943.

Date of Study: November 1942 - January 1943

Prepared by: James S. Strong, Ensign, USNR

Reviewed by: Allen L. Alexander, Sr. Chemist, Chief of Section

P. Borgstrom, Head Chemist, Superintendent
Chemistry Division

Approved by: A. H. Van Keuren, Rear Admiral, USN, Director

Distribution: BuAero (5)
BuShips (2)
Coor. R. & D. (2)

TABLE OF CONTENTS

Subject	Page
ABSTRACT	
A. INTRODUCTION	1
B. COMMON VEGETABLE OILS	3
1. Dehydrated castor oil	1
2. Chemical modifications of oils	5
3. Blown oils	8
4. Heated oils	8
5. Distillation of oils	9
6. Steam distillation of oils	9
7. Solvent extraction of oils	9
8. Derivatives of oils	10
9. Compounds added to improve qualities of oils	12
C. NATURAL DRYING OILS OF MINOR IMPORTANCE	13
D. DRYING OILS DERIVED FROM PETROLEUM	14
E. DRYING OILS DERIVED FROM TERPENES	16
F. MISCELLANEOUS SYNTHETIC DRYING OILS	17
G. GENERAL PROGRAM FOR FURTHER WORK	19

ABSTRACT

Tung oil has been so heavily depended upon in recent years that since our sources in the Orient have been cut off by the war, the need for a drying oil of such excellent properties has become critical. The amount of tung oil produced by domestic sources is ridiculously small and a synthetic oil must be produced from an available raw material before our stock of tung oil is exhausted.

The literature and patent search which comprises this report was undertaken in order to obtain a fairly thorough knowledge of what work has been done toward developing a new and superior drying oil. Many of the processes described provide valuable methods for use in research in this field, andthe materials obtained if not of value in themselves, in many cases afford a point from which to proceed toward a satisfactory end product.

A. INTRODUCTION

The volume of research that has been carried on for many years to produce a drying oil of superior properties gives a very good idea of the difficulty of the problem which at the present time has taken on an urgent aspect because of the war. Tung oil has been so widely adopted by the paint and varnish industry that it is a strategic material now that imports of this oil are cut off it is of extreme importance to find substitutes which have its fast drying and water resistant properties.

The natural answer to the problem is to produce tung oil here in this country and this is being done today on an extremely small scale. However, the enormous quantities of oil utilized in this country makes such a venture a long range one by the size of the project alone and in addition, tung trees must be seven to eight years old before oil is produced in any appreciable amount. The normal consumption of tung oil is about 120,000,000 pounds and with a record crop in 1942 there was produced in the United States about 10,000,000 pounds. The first experimentations on cultivation of tung oil trees in this country were begun in 1905 and large scale plantings were started shortly after 1920.

Thus, it is evident that during the period in which tung oil cultivation is growing more than twelve times its present rate, some product must be produced to alleviate the acute shortage of the imported oil.

The most promising possible answer to this challenge is dehydrated castor oil which possesses very attractive properties, but is not as fast drying as tung oil. This is not a new oil, however, the first process being patented about the turn of the century. A number of processes have been developed and patented since that time. However, use of this oil on a large scale did not begin until around 1936, and somewhat over 3-1/2 million pounds were used in 1939. One point which should be pointed out is that nearly all of our castor seeds and oil are imported and so the supply is not as certain as might be desired, and periodical shortages are to be expected.

There are a number of domestic oils which could be looked upon as potential substitutes if they could be modified so that their chemical constitution would more closely resemble that of tung oil. These are, linseed, soya bean, cottonseed, corn, marine and sesame oils. Since they are glycerides of acids of the same carbon skeleton and differ only by being more highly saturated than tung oil, the obvious course is to remove the hydrogen atoms in order to erase this difference. However, this has proven to be a very difficult task which has not yet been satisfactorily accomplished. Linseed oil contains an appreciable amount of linolenic acid which has three double bonds, but they are not conjugated as in tung oil. Many attempts have been made to isomerize

the linolenic acid in linseed oil to eleostearic acid as in tung oil but no important method has as yet been patented.

Petroleum has offered various products from time to time that show the property of polymerizing in air. The chemical structure of these materials does not resemble that of the vegetable oils from the standpoint of their being glycerides but the part of the molecule responsible for the polymerization is usually the same, i.e., conjugate unsaturation.

The above sources present large quantities of material and this is of prime importance if any process for manufacturing a drying oil is to be of real value. Other processes and other starting materials have been developed and new natural drying oils, polymers of acetylene, unsaturated esters of cellulose and terpene polymers are examples of some of the main groups of these secondary sources in which the supply is limited.

A complete review of the United States Patent Literature concerning drying oils is a rather formidable task, but a fairly extensive survey of the work which has been patented can be obtained from bibliographies found in some of the important books which include chapters on the subject and in articles which frequencly appear in journals of the paint and varnish trade. These are, of course, secondary sources to the classified patent file which is maintained in the search room of the Patent Office. It was in this way, therefore, that the present material was derived not with a view of absolute completeness but of practical thoroughness.

The patented work in this field quite naturally divides itself into a number of main topics, chief of which are: products derived from common vegetable oils, natural drying oils of minor importance at present, drying oils derived from petroleum, drying oils prepared from terpenes, and a miscellaneous group of purely synthetic substances not included in the other topics. By far the largest group is the first and this is conveniently broken down into several smaller groups including dehydration of castor oil, chemically modified oils, blown oils, heated oils, distillation of oils, steam distillation of oils, solvent extraction of oils, derivatives of the oils, added compounds to improve quality of oils, and methods of shortening the bodying time of a drying oil. This is the order in which these topics are discussed.

Many patents describe their product as being a very fast drying oil with superior film characteristics while others give actual drying times with or without driers as compared to linseed oil. A few go so far as to run comparative accelerated tests on films of the material, but since so many have no definite data along this line there is no real value in giving any. Therefore, all data describing the qualities of the oils produced will be omitted.

B. COMMON VEGETABLE OILS

1 Dehydrated Castor Oil - The structure itself is of ricinoleic acid which occurs to the extent of about 85% as its glyceride in castor oil suggests the method of dehydration as a means of converting it into a drying oil. In 1898 and 1901 Noerdlinger

$$CH_3 (CH_2)_4 CH_2 - CH - CH_2 - CH = CH (CH_2)_7 COOH$$
$$OH$$

was issued patents on a method of heating castor oil to 300°C until 5-10% had distilled off. By this means he dehydrated the oil to form the diene. This was a very crude method but it was not until 1934 that Scheiber (1) dehydrated ricinoleic acid by heating with a catalyst such as alumina, fuller's earth, silica gel, iron oxide or metallic iron to 200°C in a vacuum. The dehydrated acids were then reesterified with glycerol to form a new drying oil. In a similar manner Pelikan, Schuelke, and Gerkens(2) employed an acid bleaching earth known as "Tonsil." This they used in amounts of from 10-20% and the heating was carried out with agitation for 1 - 3 hours at 200-250°C. China clay was found to be an active catalyst by Cherry(3) and 5% was added to the oil which was heated at an increasing rate, while agitating with CO_2. The reaction began at 225°C and ended at 270°C after about two hours' time. The product was subsequently washed with alcohol to reduce the acid and acetyl values.(4)

A well-known dehydrating agent is sulfuric acid and Schwarcman(5) utilized this reagent by heating castor oil with 0.08% sulfuric acid at 540°F for two to three hours under a slight vacuum of 26-29 inches. Auer (6) accomplished the same end by using a stock 10% sulfuric acid in castor oil mixture which he added to castor oil to the extent of 5% and heated in vacuo while maintaining a stream of carbon dioxide. As a modification of this method he added 9% fuller's earth to act as absorption catalyst, (7) and first allowed the sulfuric acid to be absorbed on the fuller's earth before adding to the castor oil.

There are a large number of other dehydrating agents which are commonly used in organic chemistry and which have been applied to the dehydration of castor oil. Ufer(8) used 0.4% of sodium bisulfate or phosphoric acid and heated to 200 - 250°C in vacuo. Priester(9) also used 2% sodium bisulfate at atmospheric pressure and 200-250° and .15% sulfuric acid in vacuo at 170-220°C. After heating with the catalyst to effect the dehydration he added 1% of glycerol or sorbitol and esterfied the free fatty acids by heating at 270-280°C. Another catalyst used by Preister(10) was potassium persulfate which he applied not only to castor oil but hydrogenated castor oil also. The amount of catalyst used in this method was 0.3-0.4%.

A mixture of anhydrous magnesium sulfate and phosphorus pentoxide in isobutyl alcohol was employed by Sorenson(11) and the water of dehydration was removed by distilling with petroleum naphtha as a carrier. The amounts of catalyst were 0.25% phosphorus pentoxide and

5% magnesium sulfate. Rheineck and Crecelius[12] accomplished the dehydration with tungstic acid as catalyst by heating up to 260°C under a vacuum or from 240°-290°C using mineral spirits to carry away the water as it was formed. Boric anhydride was then found by Colbeth [13] to be an effective catalyst for castor oil and also acetylated castor oil when present to the extent of 1%. The process is carried out by slowly heating in vacuo to 260°C and then increasing the rate until 300°C is reached. In this case some volatile acids and heptaldehyde are carried over as well as water.

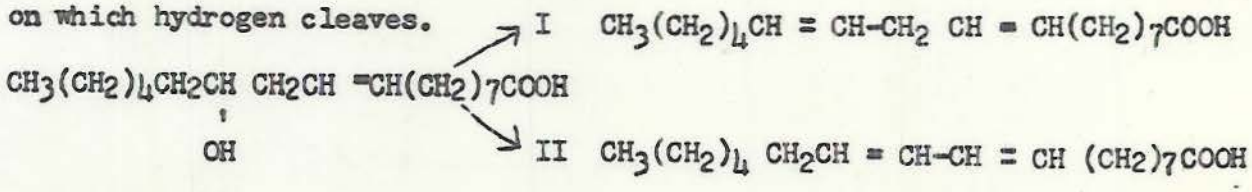
Auer[14] effected the dehydration by heating castor oil containing 0.3% of salicylic acid for 5 hours in an open kettle or 5% 2,5-di chlorobenzene sulfonic acid for 5 hours in vacuo at 260°C or with p-toulene sulfonyl chloride in the same manner. In the latter case the heating was done only at atmospheric pressure and at the end of one hour nine times the amount of castor oil was added and the heating continued for 4 hours at 250-270°C and finally one hour at 200°C. An atmosphere of nitrogen was maintained throughout the process. Only 0.1% of camphorsulfonic acid was found to dehydrate castor oil at 440°F by Schwarcman[15]. Trace amounts of methionic, ethionic, ethyl sulfonic, and methane trisulfonic acids were found to be very good catalysts by Preister [16] for example 0.004% methionic acid caused the reaction to begin at 150°C while passing a stream of carbon dioxide through the oil, and reaction is complete when the temperature had reached 235°C, which requires about 4 hours. Glycerol or sorbitol were added in 1-2% amounts and heated at 180-225°C to reduce the acid number.

Turkey red oil being an industrial product derived from castor oil by sulfonation provided a convenient means of dehydration. Thus, Pelikan, Schuelke, and von Mikusch-Buchberg[17] heated the sodium or potassium salt of sulfonated castor oil to 200-210° in vacuo with agitation by nitrogen.

The pyrolysis of an ester often leads to the dehydration product of the alcohol present and so Priester[18] formed the estolide of ricinoleic acid by heating at 250°C, then raised the temperature to 290-315°C and applied a vacuum to dehydrate and distill the product. The acid thus formed was subsequently esterfied with glycerol. Brod[19] first acetylated castor oil and pyrolysed the product at 250°C under a vacuum while passing a stream of carbon dioxide through the mixture. The phthalic ester was formed and pyrolysed by Ubben and Price [20] by heating castor oil containing 2-1/2% phthalic anhydride to 545°F for six to seven hours under reflux. The ester so formed was pyrolysed during the later stages of this heating by removing the reflux condenser in order to allow the water to escape.

The various processes described above all have the same compound as the desired end product. Unfortunately, however, there are hydrogen atoms on each side of the carbinol group so that when the water is split out the double bond is either isolated or conjugated depending

on which hydrogen cleaves.



Catalysis makes a great deal of difference in the relative amounts of I and II which are formed and determinations of diene numbers using maleic anhydride have shown that in most cases more than twice as much I than II is formed. The fast drying qualities are due to II and so the volume of the patent literature on this subject is not in search of a catalyst merely for dehydration, but one which will lead to a higher percentage of the conjugate isomer.

2. Chemical Modification of Oils - A large portion of the patent literature on synthetic drying oils is devoted to the conversion of non or semi-drying oils or improving the drying properties of drying oils by some physical treatment or addition of small amounts of various compounds. In these cases the oil itself is not altered to any great extent and the process is usually only one step, which from a manufacturing standpoint is of great importance. The raw materials in these processes are oils which are available in commercial quantities so that there is much in favor of this type of process if it results in a good or improved drying oil.

Many of the early attempts to improve the drying quality of linseed oil were crude as in the case of the patent by Clarke(21) in which the oil was stirred in a lead tank with lead shot added. This, of course, amounted to adding a lead drier and so actually was of some value. Heating linseed oil with sodium ethoxide or butoxide was found by Burr(22) to result in some isomerization to the conjugated structure which they demonstrated through infra-red absorption spectra. The procedure consisted in heating the linseed oil fatty acids with five times their weight of a 20% solution of the sodium alcoholate in the same alcohol for 24 hours.

Auer(23) found that by heating linseed oil with various aromatic sulfonic acids a modified drying oil was thereby produced. Thus, bodied linseed oil was modified by heating with 5% of its weight of benzenesulfonic acid at 140-150°C for two hours. Likewise, air blown linseed oil containing 5% of p-toluenesulfonic acid was heated at 140-150°C for 3 hours. As in the case of castor oil Auer (14) found that linseed oil, to which 5% of 2,5-dichlorobenzene-sulfonic acid had been added, was modified by heating for five hours at 290-310°C in an open vessel. An extension of this method consisted in first heating one part of linseed oil with 5% of p-toluenesulfonyl chloride at 270°C for one hour, then adding nine parts more of linseed oil and continuing the heating operation for 5 hours more while bubbling nitrogen through the oil. Salicylic acid can also be used as the catalyst in plate of the sulfonic acids by heating for two hours at 300-350°C.

Bruson[24] found that molar quantities of linseed oil and 2,4,6-tris-acetoxymethylphenyl acetate heated with 2% rosin at 250°C or with .5 - 1% of sodium ethoxide, zinc oxide, litharge, or zinc chloride at 175-200°C for four hours resulted in a loss of acetic acid and the formation of a new oil.

Many of the methods of modifying vegetable oils to impart drying properties to them were general methods applicable to nearly any oil consisting of unsaturated glycerides. Thus Dyer[25] boiled a vegetable oil for one half hour with 5-10% alcohol added. Auer [26] used small quantities (5%) of inorganic materials such as equal parts of magnesium peroxide and disodium phosphate, ammonium iodide, sodium bromide, sodium bisulfate or phosphorus pentoxide and also cresol for modifying various oils such as rapeseed, linseed, castor and soya bean oils. The temperatures varied somewhat but were usually 300-350°C and this was maintained for two hours. Oils such as linseed, soya bean, cotton-seed, corn and peanut oil were heated with 1-1/2% of calcium hypochlorite at 75°C for 5 hours in a process patented by Taylor (27). Scheiber (28) described a number of processes which included the treatment of linseed oil with 1% sulfuric acid accompanied by heating to 300°C for 4 hours and soya bean oil containing 2% ferrous iodide was heated first at 250°C for four hours and then two to three hours at 300°C. The common oils of the drying or semi-drying class were found to dissolve sulfur and Gardner (29) incorporated .05% of sulfur or selenium in a vegetable oil heated to 290°C and then desulfurized or deseleniumized the oil with copper, zinc, iron, nickel, monel metal, or oxides of lead zinc or copper. About 5% of these materials were used.

Hodgins (30) turned to oxidation as a means of modifying unsaturated glycerides and employed potassium permanganate to the extent of 1% with a trace of alkali, 1.5% sodium dichromate with a trace of alkali, 0.2% nitric acid or 1.5% benzoyl peroxide with 1% hydrochloric acid. A small amount of water (5%) was added and the mixture blown with air at room temperature for one to two hours. The decomposition products so formed were removed by filtration.

Boron fluoride has been used as a condensation catalyst in organic chemistry rather frequently and Eichwald (31) digested various vegetable oils with 2% of this reagent for 50-80 hours at 70-80°C. The catalyst was then removed by washing out with alcohol and then heating to drive the dissolved solvent out.

As an extension in the process for dehydrating castor oil, Colbeth (32) oxidized soya bean oil which contained 3% boric anhydride with air, then heated in vacuo to 260° slowly and then up to 300° rapidly.

A large amount of work has been done on the isomerism of linoleic and linolenic acids, to the conjugated structure by means of alkali treatment. The course of this isomerization can be readily followed by infra-red or ultra-violet absorption spectre and much of the work has been published in scientific literature rather than patented.

However, McKinney (33) obtained a patent on the process of heating vegetable oils with 0.1% alkali for 2 - 18 hours, and the use of alkoxides has been mentioned with regard to linseed oil (23).

The addition of halogen to an unsaturated linkage can be used to increase unsaturation by removing the elements of the hydrogen halide, thus leading to two double bonds where there was formerly only one. Of course, the alternative split is to form the triple bond is perfectly possible. Gardner (34) chlorinated vegetable oils in the presence of a ferric chloride catalyst until a 5-15% increase in weight had occurred. Dechlorination was effected by heating to 220-250°C and this operation was continued until 40-60% of the chlorine had been expelled. A small amount (1%) of coppered-zinc promotes this reaction and also aids in polymerization of the oil thus formed. Scheiber (28) carried the chlorination to 20-25% and dechlorinated with metallic zinc.

A direct method of increasing unsaturation in oils is to add a catalyst composed of nickel supported on kieselguhr and heat at 255°C. At the same time a gas such as nitrogen, carbon dioxide, or carbon monoxide is bubbled through the oil. The last named gas is the best, leading to a 20% increase in unsaturation. This is a process described by Levey (35). With the highly unsaturated oils he first hydrogenated to an iodine number of about 90 and dehydrogenation then increased the iodine value to 140. Hydrogenation directly to an iodine value of 140 did not yield the same product.

Irradiation of the oils was attempted and Long (36) irradiated drying or semidrying oils by the use of a Coolidge tube. Another example of irradiation is the use of ultra-violet light on vegetable oils containing a plant pigment or oxidizing dye such as magnesium or iron chlorophyll, fluorescein, malachite green or eosin. The pigment was present to the extent of 1 g. in five gallons. The oil was agitated with air throughout the process. This is described in a patent by Coe (37).

Because of their low price, fish oils have commanded the attention of drying oil research but the chief difficulty with these oils is that there is a rather large amount of saturated and mono-olefinic acids which results in a soft and permanently tacky film. Weeber (38) treated fish or train oil with soda lye at 65°C by allowing the mixture to stand for two days undisturbed after a primary mixing. The oil skimmed from the top was used as a drying oil. A mixture of kerosene and fish oil (100:30) to which 1-1.5% of sulfur chloride has been added was stirred continuously for 18-24 hours during which time the temperature slowly rises and falls. Levenhagen and Evans (39) claimed that the kerosene and fish oil are both altered in this process since neither acts the same alone nor, when so treated, they are mixed. Treatment of marine oils with small amounts 0.05-2% of potassium permanganate was resorted to by Hassard (40) in order to convert them to a more satisfactory drying oil.

There is much more material in the patent literature pertaining to marine oils, but in most cases a separation of constituents is effected and so these fall in another part of this study.

(3) Blown Oils - Blowing an oil with a stream of air is a very common operation. In many cases its function is merely to keep the material agitated, but very often it is a means of oxidation and a number of elaborations to the simple process have been devised and patented. Bonney and Egge (41) washed the linseed oil with low boiling petroleum ether after blowing for 10-25 hours at 80°. The usual .04% cobalt drier wasadded to promote oxidation. Long and Ball (42) carried the blowing step to 300 hours at 127°C in order to get a linseed oil compatable with nitro-cellulose. Humid air was found by Novak (43) to be more efficient than dry air and also effected a bleaching. In this process the oil is blown with humid air at 65-70°C for about twelve hours at which time the bleaching effect is over. Then the temperature is lowered to 40-45°C and blown until a rise of .004 in the refractive index has occurred. Corkery (44) passed air into soya bean oil held at 300°F until it was nearly gelled. This required about 12 hours. He then added an equal amount of soya bean oil and continued the blowing for six hours. In another patent Corkery (45) used soya bean oil which had been bodied by heating to 500-600°F for 25 hours. Half of this was blown for 17 hours at 250°F the other half added and the blowing was continued for five hours. Fish oil was treated by the same process except that the bodying time was only an hour and a half and the blowing time twelve hours.

An isolated case of blowing an oil with a gas other than nitrogen, air, or carbon dioxide is described by Waterman and Vlodrop (46) in which linseed ,soya bean oil, or sardine oil is heated to 290-300°C for one hour while passing sulfur dioxide through the oil. The oil is finally freed of sulfur dioxide by blowing with nitrogen or carbon dioxide or evacuation while still hot. This process has the effect of shortening the bodying time.

(4) Heated Oils - A number of methods have been devised whereby the oil is heated under relatively high pressures in an autoclave. Thus Kaempfe (47) selectively saponified fish or train oil by heating with 15% of water and a trace of an alkaline catalyst in an autoclave for one hour at 30 lbs., 1-1/2 hours at 15 lbs. or 3-1/4 hours at 10 lbs. The saturated and monoolefinic acids are saponified first and can be either crystallized out or driven out with superheated steam. Reese and Taggert (48) passed a vegetable oil through a tube heated to 675°F under a pressure of 400 lbs. By this means they obtained an oil of increased iodine number. After initial saturation with carbon dioxide, addition of 1/2% chlorine or 3% nitric acid in acetone. Flugge and Evans (49) passed linseed oil through a heated coil under pressure. The coil was 5/32" in diameter and was kept at a temperature of 700°F and the pressure was regulated to allow the passage of 4 ounces a minute. The coils were made of either aluminum or copper. Very high pressures were employed by Fawcett, Gibson, and Perrin (50)

who heated linseed or soya bean oil to 325°C under 3000 atmospheres for an hour and a half. Linseed oil acids were also treated in this process for three to four hours and then esterified with glycerine after removal of the saturated monomeric acids by molecular distillation.

(5) Distillation of Oils - Distillation is a very good means of effecting the removal of the saturated and monoolefinic acids because they do not polymerize and so remain lower boiling than the more highly unsaturated partially polymerized constituents. Scheiber (51) found that if ricinoleic acid is distilled in vacuo until 70-80% has been driven off, a residue remains which possesses the properties of a drying oil. Molecular distillation of a bodied linseed oil was the basis of a process developed by Osterhof, Vlodrop, and Waterman (52) The oil was bodied by heating at 285-290°C under 2-3 mm pressure for nine hours and was then distilled at 200-250°C at 10^{-5} mm pressure until about 20-30% had distilled. A similar treatment was applied to sardine oil by Fawcett and alker (53). The oil was bodied at 290-300°C under 2-5 mm pressure and distilled at 240° at 10^{-5} mm.

(6) Steam Distillation of Oils - Rather than resort to vacuum to lower the distillation temperature, steam distillation can be used. In the case of these very high boiling oils, however, superheated steam is necessary in order to make the process practical. Kaempfe (58) first bodied train oil by heating to 235-240°C for two hours and then passing steam through the oil which entered at 375-400°C but kept the oil at about 260°C. This operation is continued for 25 hours. A vacuum can be applied to facilitate the process. A small percentage (5%) of fatty acids added after the distillation, prevents gelation of the oil. In a somewhat similar manner Kaempfe heated fish oil to 280°C whereupon the temperature rose spontaneously to 350° over a period of 1-2 hours. About 5-8% of the weight distills as glycerol, acrolein, etc. After the temperature has fallen to 285°C superheated steams at 375°C is passed through for 20-30 hours with or without vacuum. These processes depend on the fact that the saturated glycerides hydrolyze more easily than the unsaturated ones. Castor oil ferment can be added to the extent of 6% along with 30% of water and 0.2% manganese sulfate. The mixture is held at 23°C for 15 hours. At the end of this period the saturated acids are separated by crystallization or by steam distillation at 250-275°C. Thurman (58) used a vacuum of 29 inches and a temperature of 600°F while passing steam through the oil for six hours.

(7) Solvent Extraction of Oils - The other method for the separation of saturated and monoolefinic acids from the more highly unsaturated constituents is solvent extraction or the distribution between two immiscible solvents after partial polymerization by heat. Behr (54) polymerized sardine oil by heat and extracted twice with nine volumes of acetone. The oil was drawn off and freed of acetone by heat. Furfural proved to be an excellent solvent for this purpose and Freeman (55) extracted raw linseed oil with two volumes of this solvent at 106°F. A second extraction was made with moist furfural which bleaches the oil. The furfural is then stripped from the oil by steam distillation up to 300-400°F. The use of 25% phenol in the furfural dissolves 70% of the oil. The addition of water and lowering

the temperature to 68°F throws the oil out of solution. Freeman (56) also made a very thorough study of pairs of immiscible solvents for use in this connection. Petroleum ether and furfural caused a marked increase in the iodine number of the oil in the furfural and an extract of the oil with ethyl acetoacetate when evaporated or diluted with water yielded an oil possessing a higher iodine number. The ethyl acetoacetate extract can also be shaken with methyl or ethyl alcohol containing 15-30% phenol. A very similar method was described by Goss and Johnstone (57) using petroleum ether and furfural.

(8) Derivatives of Oils - A more or less radical departure from the original structure of the oil was taken in a number of cases and a totally different material was obtained thereby. One of the simpler types is the substitution of some polyhydric alcohol for glycerine. Pentaerythritol was esterified by Arvin (59) with linseed and soya bean oil acids by heating to 250°C with 0.05% litharge while blowing with carbon dioxide. Rheineck, Rabin, and Long (60) used linseed oil acids which had been blown for 12 hours at 50°C. From these acids they prepared the acid chlorides by heating with PCl_3 for one hour separated and blown with carbon dioxide to free it from hydrochloric acid. Dextrose was then added followed by a slow addition of pyridine with stirring. Finally it was washed with water and methanol and freed of solvent by blowing with carbon dioxide at temperatures below 100°C. Polyglycerol is an ether of glycerol which can be prepared by heating glycerol with 1% sodium hydroxide under reflux or vacuum in an inert atmosphere. This was described in a patent by Harris (61). A nearly identical method was employed by Bruson (62) except that 25-30% of the material was allowed to distill off. Eckey (63) prepared the monostearyl glyceride and formed the polyglyceryl derivative at the same time by heating equal parts of stearic acid and phenol (10 parts) with 13 parts of glycerol, and 6 parts of toluene. A trace of sulfuric acid served as catalyst. The apparatus was fitted so that as the toluene distilled it was returned to the mixture but the water retained in a trap. The operation required three hours during which time the temperature of the mixture rose from 131°C to 143°C. The acid was then neutralized with disodium phosphate, the phenol and toluene removed by means of steam and the product was freed of salts, glycerol, and polyglycerols by washing with water. Polyglycerols can also be formed using sodium acetate as catalyst as was described in a patent by Strauss (64) in which glycerol with 1/2% sodium acetate was heated to 280° for an hour and a half, then distilled linseed oil acids were added; fifty parts of acids to seven parts of polyglycerol and heated at an increasing rate beginning at 170° and ending at 300°C while agitating with carbon dioxide. In all the above cases the polyglycerol or its derivative which was formed was esterfied with some drying oil acids. Strauss also found that sorbitol can be made to form this type of compound.

According to a patent issued to Brooks and Padgett (65) ketones prepared from linseed oil acids are drying oils. They prepared these by two methods. One consisted in the dry distillation of lime soap at 20mm

pressure and the other consisted in passing the vapors of the acids over a catalyst such as manganous oxide, ferric oxide or alumina at 400-500°C.

The incorporation of the methacrylic radical into a vegetable oil gives rise to an oil containing a good polymerizing group. Barrett and Strain (66) prepared soya bean oil diglyceride by heating the oil (mol) with glycerol (.5 mol) at 200°C for two hours, and decolorizing with activated charcoal. This material was then refluxed with 4 mols of methyl methacrylate, benzene and hydroquinone in such a way that the catalyst which is .2 mol of sodium dissolved in methanol could be added directly onto the surface of the liquid. The methanol was distilled out as the benzene binary. This required about 35 hours. The product is then dissolved in ether and washed with water and 10% sodium hydroxide to remove the hydroquinone which would retard polymerization. The ether solution was then dried over magnesium sulfate, concentrated and the residue filtered with "Filter Cell."

Hubbuch (67) prepared the linseed or soya bean monoglyceride from which he made a partial phthalic ester using phthalic anhydride and glycerol. Finally methacrylic anhydride was allowed to react with the remaining free hydroxide groups in the mixture. The patent also described the method for preparing the methacrylic anhydride in about 75% yield from potassium methacrylate.

Tthe Diels and Alder reaction has been applied to compounds possessing a conjugated diene system by condensation with maleic anhydride or compounds of that type. For instance, eleostearic acid will condense very easily with maleic anhydride and provides a method of determination of the amount present. Clocker (68) was granted a number of patents involving a process of condensations between linseed oil and maleic anhydride or α,β-unsaturated acids such as crotonic acid and citraconic anhydride, or vinyl acetate. The essential features of process included heating nine parts of linseed oil with one part of maleic anhydride in an autoclave at 250-260°C for one hour. This material can then be used as such or esterified with ethylene glycol or glycerol at 180°C and one process converted the oil into a modified bakelite by heating with xylenols and hexamethylene tetramine.

It is well known that a trihydric alcohol is paramount to a good drying oil and Bradley (69) working with this in mind made the aluminum salts of linseed oil acids and found it to be a rather stiff plastic substance with drying properties. The product was formed by first preparing the potassium salt or linseed oil acids in alcohol by refluxing molar quantities for 1/2 hour. Then this is added to a slight molar excess of aluminum chloride in four parts of water, which leads to the resinous precipitate.

The manner of binding the two or three unsaturated chains together apparently has little effect on the drying properties of the substance as evidenced by the work of Werntz (70) in which chinawood

oil was reduced by the well-known Beauvault-Blanc reduction using sodium and alcohol. A method is described whereby the oil is dissolved in xylene, toluene, or a petroleum fraction and this is added slowly to a suspension of finely divided sodium due to rapid agitation in toluene at a temperature just above the melting point of sodium. The ratio of ester group to sodium, to alcohol is 1:6:4 or 1 mol of glyceride to 18 mols of sodium to 12 mols of alcohol. The mixture is washed with water at the completion of the reaction and finally the solvent is removed leaving the alcohol.

To prepare the esters from methyl phthalate or citrate the alcohols were dissolved in toluene and the ester is added along with litharge as a catalyst and distillation through a fractionating column yielded the methyl or ethyl alcohol as a binary with toluene. Filtration, steam distillation, and solution in ether finally yielded the desired ester.

(9) Compounds Added to Improve Qualities of Oils - Small quantities of various compounds have been found to improve the quality of films of some of the drying oils. For instance, Delaney (71) found that a small amount of halowax decreased the water permeability of a film and also improves its water resistance while shortening the drying time. Sibley (72) added 0.173% of various ketones and amines and obtained faster drying and better weathering qualities of films thereby. By the addition of 0.05 - 0.75% of alkyl or aryl phosphites Cheetham (73) was able to cook varnishes which were distinctly lighter in color than when such compounds were absent. Oxalic acid was found to prevent discoloration of linseed oil on standing when it was present to the extent of only 0.02-0.1%. This was discovered by Amthor and Zinzalian (74). Reynolds (75) found that skinning of varnishes was prevented by di-n-butylcyanamide and the film formed from the varnish possessed enhanced weather resistance. Phenyl propiolic acid has the property of improving the drying quality of linseed oil. This was described in a patent by Chiwala, Waldmann and Martina (76) in which they used this compound with boiled linseed oil in a concentration of 0.04%.

As another phase of this kind of treatment of oils there are several groups of compounds which, when present in vegetable oils, shorten the time of heating necessary to body the oil to the proper viscosity. The most important of these substances are of the aromatic type containing three or more condensed rings. Schwarcman (77) used 0.05-0.1% of oxidized retene, chrysene, or picene for this purpose. A -carboxylic-anthranhydorquinone also served to shorten the bodying time of soya bean oil when present in only 0.03% quantity according to Schwarcman (78). Sorenson and Konen (79) found that anthraquinone, anthraquinone diacetate, -hydroxyanthraquinone, alizarin, -chloro-anthraquinone, phenanthraquinone, -methylanthraquinone, and nitro-anthraquinone were active catalysts for shortening the bodying time. There were many other active compounds but acid groups were said to retard the effect. Some of the same compounds are included in a patent by Auer (80). This list included fluorescein, anthraquinone -sulfonic acid, amino-G-acid, 2-aminoanthraquinone, 1-naphthylamine-3:6:8 sulfonic acid, -chloroanthraquinone, anthrahydroquinone diacetate, and naphthalene tetrachloride. The quantity used in this case was 1%.

In another patent Auer (81) added nitroanthraquinone and -nitroso--napthol to the list.

Other groups of compounds were found to have the ability to shorten the bodying time of an oil and amines are among the most important of these. Arsem (82) used 1% of benzidene, p-toluidine, diphenylamine, p-phenylenediamine, m-phenylenediamine, and diisopropylamine. The amines were also recognized by Auer (83) who used -naphthylamine, diphenylamine hydrochloride and diphenylamine trichloroacetate.

Aromatic sulfur compounds are effective bodying agents as Bradley and Johnston (84) found in the mercaptans. Examples of the type are -naphthol mercaptan, p-thiocresol, thiosalicylic acid. These were used in 0.1% concentrations. Parkin (85) used diphenyl-disulfide in 0.2% concentration.

Small concentrations of castor oil were found to shorten the bodying time by Gin (86) who prepared a stock solution of castor oil in linseed oil. This was made from 16 parts of heavily bodied linseed oil, 7 parts of refined linseed oil and 8 parts of castor oil. Then 15 parts of this stock was dissolved in 85 parts of linseed varnish oil and bodied by heat. The effective concentration of castor oil in this case was about 1/2%.

A quicker bodying was observed by Auer (87) when linseed oil containing 5% sodium bisulfite was subjected to a potential difference of 230 volts between electrodes 1/2 inch apart. The temperature employed in bodying was 300°C.

C. NATURAL DRYING OILS OF MINOR IMPORTANCE

It is only natural to suppose that there are plants in existence which produce oils composed of the unsaturated acids necessary to exhibit drying properties. This has been found to be the case in several instances. However, discovery of such a source and expansion to a commercial scale is a problem of considerable size. Nevertheless, a number of such oils warrant mention here as substitutes for tung oil.

A very common beverage among the people of Mexico is produced from the plant known as chia or Salvia Hispanica of the Labiatial family, and seeds from this plant produce an oil which is called chia oil. This oil was patented as a drying oil by Lomanitz (88). Its high iodine value (187.59) is evidence of its degree of unsaturation.

The shell of the cashew nut contains a liquid which has a pronounced vesicant action on the skin. However, this property can be destroyed by heating with dilute mineral acid. When this liquid is heated in a copper kettle to 100°C first to drive off any water and then to 200°C for the period long enough to obtain the desired viscosity

(1/2-4 hours) a typical drying oil is then prepared. This is a method which was described by Harvey (89) and another method is to blow air through the liquid while heating at 500°F. A modified oil can also be prepared by allowing a mixture composed of 90% cashew shell liquid, 9% formalin (40%) and 1% manganese resinate to stand for a day.

Bangar nut oil which comes from the nut of Sterculia foetida appendiculata, and chica is a drying oil which is found in the Phillipines. It can be bodied at 600°F and blended with the common drying oils. Harvey also patented this oil (90).

The oil from the inner kernel of the nut from the chinese tallow tree (Sapium sebiferum) is a drying oil. It is native to the southern states and is quite abundant near Houston, Texas, according to Quinby (91) who obtained a patent on it.

Priester (92) devised a method of safely bodying Isano oil. This is the oil found in the kernel of the nuts of "Origokea Klaineane" which belongs to the family of the Oleaceae. It is frequently found in tropical Africa and elsewhere as well. The oil has been known to be of use as a drying oil, but it could not be bodied because heat treatment starts an exothermic reaction which oftens leads to an explosion. A mixture of 30 parts of Isano oil and 70 parts of linseed or soya bean oil are heated for one hour at 250°C. In this way it is boiled with no trouble whatsoever.

D. DRYING OILS DERIVED FROM PETROLEUM

Petroleum provides an unlimited source of raw materials from which drying oils might be manufactured. This is the opposite of the case of other natural drying oils where the drying ability was already present but the supply limited, because in petroleum the drying ability is not initially present while the supply is abundant.

By far the predominating method used for converting petroleum fractions into drying oils is by chlorination and dechlorination. According to Thiele (93) kerosene which contains cycloparaffins is chlorinated until its density rises from 0.814-0.816 to 1.200. It is then washed with water and mixed with 40% of the original weight of acetic acid and the mixture is poured on zinc-copper couple. The reaction is vigorous and during the course of the reaction changes in color from black to amber. The resulting oil is then washed with water and sodium carbonate solution and finally filtered through fuller's earth or sawdust.

The preparation of drying oils from mineral oils is fully described in several patents by Gardner (94) and Bielouss (95) or both (96). The main features of the various methods given is chlorination to an oil containing 28-34% chlorine and dechlorination either by heating to 220-230° alone for ten hours, or to 180-210°C with various catalysts such as a mixture of 15 parts iron filings and one part aluminum powder, 18 parts zinc dust and one part copper, or sixteen parts magnesium oxide. The chlorinated oil can

can also be dechlorinated by passing superheated steam at 170-180°C through it in either the presence or absence of small amounts of iron, zinc, copper, magnesium oxide, zinc oxide, or cupric oxide. The oil thus prepared had a tendency toward gelation which could be prevented by adding 25% rosin either before or after removal of the chlorine. When rosin was added before dechlorination, no catalyst was used and the oil was heated at 250°C. Mixtures of the dechlorinated oil were also made with substantial preparations of soya bean oil, castor oil, paraffin wax or hydrogenated whale oil and distilled under vacuum of 35-40 mm pressure, and a fraction boiling up to 260°C was taken from the mixtures with soya bean or castor oil but only up to 190°C from the others.

Brooks and Padgett (97) chose a petroleum fraction called "Solar Oil" which is between lubricating oil and kerosene (above 250°C). This was chlorinated to the dichloride stage and dissociated by means of barium chloride at 350-550°C in vacuo. By the chlorination of fuel oil to only 6.6% chlorine Kipper (98) obtained an oil which he passed through a tube heated to 400°C under a pressure of 30 pounds. A mixture of 90% nitrogen and 10% oxygen was passed through the tube along with the oil, and the tube was packed with asbestos fiber on which was spread an equimolecular mixture of copper chloride, iron, and copper oxide.

Another method was claimed by Dyer (99) to produce a drying oil from mineral oil. The oil which had been freed of lighter fractions such as gasoline and kerosene was boiled with 5-10% alcohol for one-half hour and dyring properties were thus imparted to it.

Cracked gasoline contains a certain amount of unsaturated fragments which may be catalytically polymerized to form a drying oil. This is the method by which Hyman (100) passed cracked gasoline vapors over a catalyst of active clay at about 175°F. About 10% of the effluent vapors are allowed to condense and this amount constitutes a drying oil. Another method used by Hyman consists in the passage of the cracked vapors over fuller's earth, silica gel or active clay at 150-650°F or treatment with dilute sulfuric acid at 200°F. The resulting material is concentrated to 50% its volume by vacuum or steam distillation.

A very similar process was developed by Bjerregaard (101) who used a 1% cerium nitrate catalyst while blowing the polymerized cracked gasoline with air. Distillation yielded 58% drying oil which could then be separated into thin, medium, and thick drying oils by redistillation up to 525°F.

Mikeska and Gleason (102) obtained a patent on a rather involved process in which the cracked gasoline was cooled to -70°F, saturated with boron fluoride, and allowed to warm to room temperature. The mixture was then washed with water and distilled up to 400°F. The residue constituted 40% of the original material and could be utilized as a drying oil as such or further distilled up to 400°F at 2 mm pressure. About 30% of the original material remained as residue and it was dissolved in benzene. Acetone was then added to the benzene solution and

thus precipitated the high polymers. Removal of the acetone and benzene yielded a refined drying oil.

E. DRYING OILS DERIVED FROM TERPENES

The terpenes are a group of compounds of whose members a number are sufficiently unsaturated to be of possible use in the production of drying oils. The most common terpene source we have is, of course, turpentine and the supply is large enough to warrant some effort toward the manufacture of a drying oil from it.

One of the early attempts at this problem was made by Hall (103) who distilled a mixture of turpentine and gum cedar or pine wood. The woody material was removed after distillation ceased at 100°C. The distillate consisted of two layers which were separated andthe oily layer was returned to the residue while it was still hot in order to keep it liquid. This mixture constituted a drying oil.

Humphrey (104) used a diterpene which was blown with air for 20 hours while heating at 150-250°C. Rankin (105) refluxed turpentine, pine oil, or dipentene with sulfuric acid, fuller's earth, activated carbon, or metallic salts such as stannic chloride or zinc chloride. Distillation to separate the material boiling below 250°C yielded an oil which was bodied by ozonizing for four hours.

A drying oil may be produced from wood rosin by the addition of p-toluene sulfonic acid (0.1%) to the rosin when molten. The temperature is held constant for one-half hour, raised up to 300°C and back down to 250°C. At this point the system is evacuated to a pressure of 2-15 mm. and an oil distills which has drying properties. This method was described in a patent by Johnston (106).

A condensation product of turpentine and phenol was the basis on which Lemmer and Hultzsch (107) based their patent. The condensing agent was hydrochloric or hydrofluoric acid and the product of this reaction was heated to 230-240°C for 12 hours with 62% of its weight of linseed oil and 0.5% of zinc oxide.

When wood is digested to wood pulp a liquid resin is obtained which is known as tall oil or talloil. This oil consists of a mixture of resin acids and fatty acids with a low percentage of unsaponifiable material. One step in the conversion of tall oil into a drying oil is necessarily esterification.

Reppe and Wolff (108) heated tall oil to 170-225°C with 1% zinc oxide and bubbled acetylene through it and obtained a drying oil as the end product. They also used 3% zinc oxide and an equal weight of toluene. This mixture was heated in an autoclave to 180-200°C under a pressure of 15-20 pounds while a mixture of two parts of nitrogen and one part of oxygen was introduced. This addition was continued until the weight necessary for the formation of the vinyl ester had been absorbed.

In order to rid the oil of saturated and monoolefinic acids Segesseman (109) dissolved distilled tall oil in 6-1/2 volumes of acetone and cooled to -60°C for one hour. In this way 40% of the material separated as a solid. This consisted chiefly of oleic acid. The residue obtained by removal of the acetone was esterified by heating with 11% of its weight of glycerol gradually up to 280°C over a period of six hours.

F. MISCELLANEOUS SYNTHETIC DRYING OILS

Many of the oils which have been made which possess drying properties are not derived from vegetable oils, petroleum or terpenes and so must be grouped together in a miscellaneous class. However, most of the patents falling in this group have acetylene, cellulose, or unsaturated acids as their starting material and the rest which are few in number cannot be classed as anything but miscellaneous since they have nothing in common with the others.

As an example of this latter group Schlatter (110) prepared a drying oil by oxidizing coumarin with 4% of its weight of chromyl chloride in 200% carbon tetrachloride. Modifications on the original method included the presence of chinawood oil, linseed oil, and or gum dammar. The reactions were carried out below 100° C with constant stirring.

Sorenson (111) heated furylethylene with 1% benzoyl peroxide in a pressure tube at 180-190° C and obtained a light red syrup possessing drying properties.

Allenes are polymerizable substances and a series of derivatives of 1,2-butadiene with substitutions in the 4-position were prepared and polymerized to drying oils by Nicodemus, Lange and Horn (112). The polymerization was effected by boiling in the absence of air for 48 hours and distillation between 95 and 100° C at 10 mm pressure. The substitutions were - OH, $-OCH_3$, $OOCCH_3$, -CN, - SH, $- OC_6H_5$, $- NHC_4H_9$, $- N(C_2H_5)_2$, and $-SCH_3$.

The chlorination of fatty acids is a common practice, but stearic acid as a starting material for this process is somewhat unusual. Dreger, Ross, and Kirschenbauer (113) prepared a chlorinated stearic acid. The more highly chlorinated fraction was separated by fractional crystallization and dechlorinated with alkali. Steam was passed through the molten acid to sweep out the air and then soda ash or anhydrous sodium carbonate was added in small portions as the temperature was gradually raised to 250° C. This step required six hours. At the end of this period the reaction mass was dissolved in water and acidified with dilute sulfuric acid. The acids were then filtered, washed with sodium sulfate solution to remove the excess sulfuric acid, and finally esterified with glycerol.

The late J. A.Nieuwland initiated work on the catalytic polymerization of acetylene and the method of preparation was patented as well as the processes for converting the initial products of the polymerization into useful materials. The original process as developed by Nieuwland (114) consisted in the use of a catalyst prepared from 9-1/2 parts of ammonium chloride, 28-1/2 parts of cuprous chloride, 1 part of copper powder, and 10 parts of water. Acetylene was passed into this mixture while the temperature was kept below 25° C. When the catalyst mixture is saturated, the acetylene is stopped and the product is collected by distillation. The catalyst may then be used again to prepare more polymer. The chief constitutents of the product are vinyl and divinylacetylene. A higher yield was obtainable if an alternate catalyst were used composed of 38.3 parts of acetic acid (or other acid such as 80% formic acid, 68.5 parts of 85% lactic acid or a mixture of 80.5 parts of diethylaniline and 32.5 parts of 90% formic acid) 42.7 parts of pyridine, 17.8 parts of cuprous chloride, and 3 parts of copper powder. This catalyst developed by Nieuwland and Vogt (115) was used in the same way as was the original one. On distillation some acetic acid and pyridine was carried over which was removed by washing with water. The product distilled into two fractions. The first was collected at 5-10° C and was chiefly vinylacetylene and the second fraction was taken between 80 and 90° C which was divinylacetylene.

The divinylacetylene could then be polymerized by boiling in an inert atmosphere for several hours. The inert atmosphere was used because of the great tendency of the compound to take up oxygen from the air to form explosive derivatives. After the refluxing operation the unpolymerized material was removed by distillation and the residual drying oil was thus obtained. The first work in this connection was carried out by Nieuwland (116) and modifications of this method were devised by Collins (117) in which the polymers were heated to higher temperatures by sealing in a closed tube or using xylene as a diluent, and used dibutylamine as a polymerization catalyst. The first hydrogenation of divinylacetylene was also carried out by Collins with a platinum catalyst. Calcott, Carter and Downing (118) obtained a product consisting of 1,3,5-hexatriene by hydrogenation of divinylacetylene over nickel on kieselguhr until it absorbed 2-1/2% of its weight. This product could thus be purified by distillation at 75-80° C and polymerized in the same way that the divinylacetylene was; by refluxing in an inert atmosphere for five hours. The product thus obtained boiled at 70° C at 10 mm pressure and had no explosive tendencies, but was somewhat slower in drying than the divinylacetylene polymer.

A copolymer of divinylacetylene and tung oil was produced by Lawson and Arvin (119) by heating equal parts of each dissolved in an equal amount of toluene at 125° C for 14 hours in an atmosphere of nitrogen. In another case one part of castor oil with three parts of divinylacetylene in three parts of Hiflash-naphtha were heated at 125-130° C for 9 hours in a closed vessel. At the end of this period 1/3 - 1/2 of the solvent was removed by distillation up to 100° C.

An extension of this idea was carried out by Collins (120) who refluxed 4 parts of divinylacetylene (b.p. 20-53° C/250 mm) with 1 part of tung oil and 0.07 parts of phthalic anhydride for two hours. Five parts of xylene were then added and the mixture was distilled under reduced pressure until all the unchanged divinylacetylene and some of the xylene had distilled. Finally the phthalic anhydride was then frozen out by cooling below 0° C.

The same type of reaction was carried out using 8 parts of divinylacetylene, 1 part of glycol dilinoleate and 0.1 part of maleic anhydride.

In as much as cellulose is a polymer in itself it should be possible to prepare a drying composition by attaching a group on the cellulose molecule which will polymerize in air. Malm and Fordyce (121) prepared crotyl cellulose and mixed crotyl and stearyl cellulose which they found would dry upon exposure to ultraviolet light. Such esters had been made and patented earlier in France and the process consisted in using a mixture of crotonic anhydride and acetic acid.

Hahn (122) prepared the crotyl ethers of cellulose by heating 7 parts of crotyl chloride, 1 part of cellulose, 8-9 parts of benzne, 4 parts of sodium hydroxide and 1/2 part of water in an autoclave at 140-150° C for eight hours at a pressure of 150 pounds. At the end of the heating operation the benzene and unreacted crotyl chloride were steam distilled out and the crotyl cellulose and unreacted cellulose were separated by solution in alcohol in which the crotyl cellulose was soluble.

A reasonable assumption would be that glycols and glycerol esters of crotonic acid would be capable of drying. However, Bruson (123) prepared these compounds and found that such as not the case, but instead were excellent plasticizers. Woodhouse (124) prepared glycol mono and dimethacrylate but they would polymerize only upon heating with 1% benzoyl peroxide. On the other hand, Bradley (125) found that resins made from glycol and maleic anhydride were soft but would dry with a cobalt drier.

As the above study clearly illustrates, the patent literature is full of processes for the production of drying oils. These are prepared from a variety of sources including natural oils, petroleum, terpenes, and purely synthetic substances. Many of these preparations have become important enough to be manufactured and are now available commercially while others either proved themselves to be unsatisfactory or were superceded by superior material subsequently developed.

G. GENERAL PROGRAM FOR FURTHER WORK

By examination of the methods herein described it becomes immediately evident that in spite of the volume of work which has been done, there are spaces which might be filled with the hope of arriving

at an oil of desirable drying properties. The object of this study has then been accomplished if on the basis of the commercially assigned patents we are able to obtain samples of oils produced by their processes or reasons for their not being suitable for commercial production. In addition to this the patent literature describes in detail numerous operations which are available for research in this field and suggests possibilities where further work may be carried out.

The plan for this work will follow the outline of the report in general beginning with the common vegetable oils.

Castor oil has been dehydrated in innumerable ways, but the percentage of the conjugated isomer formed in the process is always quite low, usually about 25%. Any method which increases this percentage would lead to a definitely superior product. A common reaction for the preparation of olefins in organic chemistry is the pyrolysis of a methyl xanthate of the corresponding alcohol. In the case of an unsaturated alcohol the split is said to favor a conjugated product if such is possible. It is therefore proposed to prepare the methyl xanthate of castor oil or ricinoleic acid to be pyrolyzed in order to find out whether a product containing a larger percentage of the conjugated isomer is obtained. This can be determined readily by means of the diene number using maleic anhydride as in the Diels and Alder reaction.

$$CH_3(CH_2)_5\underset{\underset{OH}{|}}{CH}-CH_2-CH=CH\ (CH_2)_7\ COOH \xrightarrow[NaOH]{CS_2}$$

$$CH_3(CH_2)_5\underset{\underset{OCSSNA}{|}}{CH}-CH_2-CH=CH(CH_2)_7\ COOH \xrightarrow{(CH_3)_2\ SO_4}$$

$$CH_3(CH_2)_5-\underset{\underset{OSCSCH_3}{|}}{CH}-CH_2-CH=CH\ (CH_2)_7 COOH\ (CH_3) \xrightarrow[heat]{\Delta}$$

$$CH_3(CH_2)_5 CH=CH-CH=CH(CH_2)_7\ COOH(CH_3)$$

There are a number of possible ways of increasing the number of double bonds in oleic or linoleic acid to three so that one could obtain an isomer of eleostearic acid. The methods are based on standard organic reactions so that the reactions involved are plausible, but, of course, such difficulties as yields and isolation may enter into make the method useless. However, the following reactions appear sufficiently straight-forward as to be worthy of trial.

Oxidation is the basis of all three of these methods the first utilizing selenium dioxide, the second perphthalic acid, and the third hydrogen peroxide in glacial acetic acid. The reactions are as

follows:

Oleic Acid

1) $CH_3(CH_2)_5CH_2-CH_2-CH=CH\ CH_2\ CH_2(CH_2)_5\ COOH$

$\downarrow SeO_2$

$CH_3(CH_2)_5\ CH_2-CHCH=CH\ CH\ CH_2(CH_2)_5\ COOH$

$OH \qquad OH$

$\downarrow -2H_2O$

$CH_3(CH_2)_5CH=CH-CH=CH-CH=CH(CH_2)_5\ COOH$

2) $CH_3(CH_2)_6\ CH_2CH=CHCH_2(CH_2)_6\ COOH$

$CH_3COOH,\ H_2O_2$

$CH_3(CH_2)_6\ CH_2\ CH\ -\ CH\ CH_2(CH_2)_6\ COOH$

$OH \quad OH$

$\downarrow -2H_2O$

$CH_3(CH_2)_6CH=CH-CH=CH(CH_2)_6\ COOH$

3) $CH_3(CH_2)_6CH_2CH=CHCH_2(CH_2)_6\ COOH$

$\downarrow C_6H_4(COOH)_2$

$CH_3(CH_2)_6\ CH_2CH-\ CHCH_2(CH_2)_6\ COOH$

$\downarrow Ac_2O$

$CH_3(CH_2)_6\ CH_2CH\ -CHCH_2(CH_2)_6\ COOH$

$OAc \quad OAc$

$\downarrow \Delta$

$CH_3(CH_2)_6\ CH=CH\ -\ CH=CH\ (CH_2)_6\ COOH$

Linoleic Acid

1) $CH_3(CH_2)_3CH_2CH = CHCH_2CH = CHCH_2(CH_2)_6\ COOH$

$\downarrow SeO_2$

$CH_3(CH_2)_3\ CHCH{=}CH - CH\ CH{=}\ CHCH_2(CH_2)_6\ COOH$

$OH \qquad OH$

$+$

$CH_3(CH_2)_3CH_2CH = CH\ CH\ CH = CH\ CH\ (CH_2)_6\ COOH$

$OH \qquad OH$

$+$

$CH_3(CH_2)_3CHCH = CHCH_2CH = CHCH\ (CH_2)6\ COOH$

$OH \qquad OH$

$\downarrow -2H_2O$

$CH_3(CH_2)_2\ CH{=}\ CH{-}CH{=}\ CHCHCH{=}CH{-}CH_2(CH_2)_6\ COOH$

$+ \quad OH$

$CH_3(CH_2)_3\ CH_2CH = CHCHCH = CHCH = CH(CH_2)_5\ COOH$

OH

$+$

$CH_3(CH_2)_2CH = CHCH = CHCH_2CH = CHCH = CH(CH_2)_5\ COOH$

2) $CH_3(CH_2)_3\ CH_2CH = CH\ CH_2CH = CHCH_2\ (CH_2)6\ COOH$

$CH_3\ COOH,\ H_2O_2$

$\downarrow$

$CH_3(CH_2)_3\ CH_2CH - CHCH_2CH = CHCH_2(CH_2)_6\ COOH$

$OH \quad OH$

$+$

$CH_3(CH_2)_3\ CH_2CH = CHCH_2CH - CH\ CH_2(CH_2)_6\ COOH$

$OH \quad OH$

$-2H_2O$

$CH_3(CH_2)_3CH{=}\ CHCH = CHCH = CHCH_2(CH_2)_6\ COOH$

$+$

$CH_3(CH_2)_3CH_2CH = CHCH = CHCH = CH(CH_2)_6\ COOH$

3) $CH_3(CH_2)_3CH_2CH = CHCH_2CH = CHCH_2(CH_2)_6COOH$

$$\downarrow C_6H_4 \begin{smallmatrix} COOOH \\ COOH \end{smallmatrix}$$

$$CH_3(CH_2)_3CH_2\underset{\diagdown O \diagup}{CH-CH}CH_2CH = CHCH_2(CH_2)_6COOH$$

$$+$$

$$CH_3(CH_2)_3CH_2CH = CHCH_2\underset{\diagdown O \diagup}{CH-CH}CH_2(CH_2)_6COOH$$

$$\downarrow Ac_2O$$

$$CH_3(CH_2)_3CH_2\underset{OAC}{CH}-\underset{OAC}{CH}CH_2CH = CHCH_2(CH_2)_6COOH$$

$$CH_3(CH_2)_3CH_2CH = CHCH_2\underset{OAC}{CH} - \underset{OAC}{CH}CH_2(CH_2)_6COOH$$

$$\downarrow \Delta$$

$$CH_3(CH_2)_3CH = CH - CH = CHCH = CHCH_2(CH_2)_6COOH$$

$$CH_3(CH_2)_3CH_2CH = CHCH = CHCH = CH(CH_2)_6COOH$$

Another phase of the projected research program is to obtain samples of the less known natural oils such as chia, isano, chinese tallow nut, bangar nut, and cashew shell oils and try them in varnishes and other formulations where tung oil is now used. It is also hoped that samples of materials covered by the patents discussed will be available, for similar tests and thus obtain a small group of oils which may be good second choices but at least the leaders in such a large number as should be available.

There are, of course, numerous reactions which may lead to easily polymerizable compounds using purely synthetic starting materials. Crotonaldehyde, for instance, can be made to condense with itself to form a polyene compound. If it were oxidized to an acid and esterfied with glycerol it might constitute a drying oil.

Glyoxal is a possible starting material because if it is allowed to condense at both aldehyde groups and water split out a conjugated diene is thereby produced directly.

Sorbic acid is rather easily prepared and contains a conjugated diene system although this is conjugated with the carboxyl group and polymerization seems to be somewhat impaired by this connection.

Any one of these paths, if followed. would undoubtedly bring one into a maze of possibilities which have good chances to lead to a solution to the problem.

1. U.S.P. 1, 942, 778 J. Scheiber

2. U.S.P. 2,209.065 K.A. Pelekan, E. F. R. Schuekle, and J. F. Gerkens to the Woburn Degreasing Co.

3. U.S.P. 2,290,165 O.A. Cherry to the Glidden Co.

4. U.S.P. 2,304,074 O. A. Cherry to the Glidden Co.

5. U.S.P. 2,282,892 A. Schwarcman to Spencer Kellogg & Sons

6. U.S.P. 2,298,916 L. Auer

7. U.S.P. 2,140,271 A. Schwarcman to Spencer Kellogg & Sons

8. U.S.P. 1,892,258 H. Ufer to I. G. Farbenindustrie

9. U.S.P. 2,226,831 R. Priester to Naamlooze Vermootschap Industrieele Maatshappij Voohien Noury and Van der Lande

10. U.S.P. 2,226,830 R. Priester to Naamlooze Vermootschap Industrieele Maatshappij Voohien Noury and Van der Lande

11. U.S.P. 2,230,549 B. E. Sorenson to E. I. DuPont de Nemours & Co.

12. U.S.P. 2,261,663 A. E. Rheineck and S. B. Crecelius to Devoe and Raynolds Co.

13. U.S.P. 2,278,425; 2,278,426; 2,278,427 I. F. Colbeth to Baker Castor Oil Co.

14. U.S.P. 2,298,914; 2,298,917 L. Auer

15. U.S.P. 2,292,902 A. Schwarcman to Spencer Kellogg & Sons

16. U.S.P. 2,195,225 R. Priester to Naamlooze Vermootschap Industrieele Maatschappij Vooheen Noury and Van der Lande

17. U.S.P. 2,198,884 K. A. F. Pelekan, E. F. R. Schuelke and D. von Mikusch-Buchberg

18. U.S.P. 2,156737 R. Priester to Naamlooze Vermootschaf Industrieele Maatschappij Vooheen Noury and Van der Lande

19. U.S.P. 2,212,768 J. S. Brod

20. U.S.P. 2,246,768 R. F. Ubben and J. R. Price to Armstrong Paint & Varnish Works

21. U.S.P. 122,439 R. F. Clarke

22. U.S.P. 2,242,230 H. O. Burr to University of Minnesota

23. U.S.P. 2,244,666; 2,298,271; L. Auer to J. R. Newman

24. U.S.P. 2,282,557 H. A. Bruson to Resinous Products and Chemical Co.

25. U.S.P. 1,256,536 W. Dyer

26. U.S.P. 2,298,270; 2,300,090 L. Auer

27. U.S.P. 1,861,514 L. D. Taylor to Mathieson Alkali Works, Inc.

28. U.S.P. 1,896,467 J. Scheiber

29. U.S.P. 1,986,571 H. A. Gardner

30. U.S.P. 2,133,894; 2,167,206; 2,196,796 F. S. Hodgins to H. R. Reichhold as Reichhold Chemicals

31. U.S.P. 2,160,572 E. Eichwald to Shell Development Co.

32. U.S.P. 2,278,425; 2,278,426; 2,278,427 I. M. Colbeth to Baker Castor Oil Co.

33. U.S.P. 2,185,414 R. S. McKinney to the United States of America

34. U.S.P. 1,452,553 H. A. Gardner

35. U.S.P. 1,374,589 H. A. Levey

36. U.S.P. 1,818,073 J. S. Long 1/3 to LeHigh University and 1/3 to Archer-Daniels Midland Co.

37. U.S.P. 2,165,130 M. R. Coe

38. U.S.P. 1,257,562 R. Weeber

39. U.S.P. 1,407,469 F. A. Levenhagen and J. W. Evans

40. U.S.P. 2,160,861 W. Hassard to D. B. Boyd

41. U.S.P. 2,040,461 R. D. Bonney and W. S. Egge to Congoleum Nairn, Inc.

42. U.S.P. 2,059,259 J. S. Long and A. L. Ball, Jr. 1/3 of Ball's to Archer-Daniels Midland Co. and 1/6 to LeHigh University

43. U.S.P. 2,178,604 I. J. Novak to Raybestos-Manhatten, Inc.

44. U.S.P. 2,248, 964 F. W. Corkery to Falk and Company

45. U.S.P. 2,248,965 F. W. Corkery to Falk and Company

46. U.S.P. 2,188,273 H. I. Waterman and C. Van Vlodrop to Imperial Chemical Industries, Ltd.

47. U.S.P. 1,122,400 W. Kaempfe

48. U.S.P. 2,113,358 F. M. Reece and H. T. Taggert

49. U.S.P. 2,120,044 S. L. Flugge and R. J. Evans to Continental Can Co.

50. U.S.P. 2,155,009 E. W. Fawcett, R. O. Gibson and M. W. Perrin to Imperial Chemical Industries, Ltd.

51. U.S.P. 1,979,495 J. Scheiber

52. U.S.P. 2,065,728 D. Osterhof, C. Van Vlodrop and H. I. Waterman to Imperial Chemical Industries, Ltd.

53. U.S.P. 2,128,354 E. W. Fawcett and E. E. Walker to Imperial Chemical Industries, Ltd.

54. U.S.P. 2,166,103 O. M. Behr to Vegetable Oil Products Co.

55. U.S.P. 2,200,390 S. E. Freeman to Pittsburgh Plate Glass Co.

56. U.S.P. 2,200,391 and 2,291,461 S. E. Freeman to Pittsburgh Plate Glass Co.

57. U.S.P. 2,290,609 W. H. Goss and H. F. Johnstone to H. A. Wallace and Successors

58. U.S.P. 1,745,877 B. H. Thurman to Gold Dust Corp. by Mesne Assignments

59. U.S.P. 2,029,851 J. A. Arvin to E. I. DuPont De Nemours & Co.

60. U.S.P. 2,077,371 A. E. Rheineck, B. Rabin and J. S. Long to Devoe and Raynolds Co., Inc.

61. U.S.P. 2,023,388 B. R. Harris

62. U.S.P. 2,284,127 H. A. Bruson to Rohm and Haas Co.

63. U.S.P. 2182,397 E. W. Eckey to Proctor and Gamble Co.

64. U.S.P. 2,197,813 F. A. Strauss to Wecoline Products, Inc.

65. U.S.P. 1,197,599; 1,220,820 B. T. Brooks and F. W. Padgett to Gulf Refining Co.

66. U.S.P. 2,160,532 H. J. Barrett and D. E. Strain to E. I. DuPont de Nemours and Company

67. U.S.P. 2,190,789 L. P. Hubbuch to E. I. DePont de Nemours & Co.

68. U.S.P. 2,188,882; 2,188,891 E. F. Clocker

69. U.S.P. 2,169,577 T. F. Bradley to American Cyanamide Co.

70. U.S.P. 2,101,227 E. J. Herntz, E. I. DuPont de Nemours & Co.

71. U.S.P. 1,980,258 M. E. Delaney to Bakelite Corp.

72. U.S.P. 2,099,236 R. L. Sibley to Monsanto Chemical Co.

73. U.S.P. 2,153,512 H. Cheetham to Resinous Products and Chemical Co.

74. U.S.P. 2,162,542 F. G. Amthor and G. Zinzalian to Wecoline Products Co.

75. U.S.P. 2,287,946 H. C. Reynolds, Jr. to Standard Oil Development Co.

76. U.S.P. 2,102,307 A. Chwala, E. Waldmann and A. Martina

77. U.S.P. 2,207,686 A. Schwarcman to Spencer, Kellogg and Sons Co.

78. U. S. P. 2,230,470 A. Schwarcman to Spencer Kellogg and Sons Co.

79. U.S.P. 2,213,935 to Archer-Daniels-Midland Co.

7
80. U.S.P. 2,298,915 L. Auer

81. U.S.P. 2,298,918 L. Auer

82. U.S.P. 1,760,535 W. C. Arsen to General Electric Co.

83. U.S.P. 2,234,949 and 2,298,919 L. Auer to J. R. Newman

84. U.S.P. 2,219,862 T. F. Bradley and W. B. Johnston to American Cyanamide Co.

85. U.S.P. 2,263,887 F. P. Parkin to Minnesota Linseed Oil Paint Co.

86. U.S.P. 2,260,140 W. W. Gin to Vegetable Oil Specialty Corp.

87. U.S.P. 2,234,545 L. Auer to J. R. Newman

88. U.S.P. 1,244,521 S. Lomanitz 1/4 to Joseph Joffe

89. U.S.P. 1,725,794 and 1,725,796 M. T. Harvey to Harvel Corporation

90. U.S.P. 1,939,773 H. T. Harvey to Harvel Corporation

91. U.S.P. 2,248,823 F. R. Quinby 1/2 to Kirk Griggs

92. U.S.P. 2,228,154 R. Priester to Naamlooze Vermootschap Industrieele Maatschappij Vooheen Noury and Van der Lande

93. U.S.P. 1,254,866 F. C. Thiele to Cudahy Refining Co.

94. U.S.P. 1,412,399 1,484,018 H. A. Gardner

95. U.S.P. 1,384,423 E. Bielouss to H. A. Gardner

96. U.S.P. 1,384,447 H. A. Gardner and E. Bielouss

97. U.S.P. 1,197,599 and 1,220,821 B. T. Brooks and F. W. Padgett to Gulf Refining Co.

98. U.S.P. 2,171,851 H. B. Kipper

99. U.S.P. 1,256,535 W. Dyer

100 U.S.P. 1,919,722 and 1,919,723 J. Hyman to Velsicol Corp.

101 U.S.P. 2,035,455 A. P. Bjerregaard to the Gray Process Corp.

102 U.S.P. 2,092,889 L. A. Mikeska and A. H. Gleason to Standard Oil Develop. Co.

103 U.S.P. 1,279,106 W. G. Hall

104 U.S.P. 1,793,220 I. W. Humphrey to Hercules Powder Co.

105 U.S.P. 1,886,586 L. P. Rankin to Hercules Powder Co.

106 U.S.P. 1,975,211 O. C. Johnston to Hercules Powder Co.

107 U.S.P. 2,284,156 F. Lemmer and K. Hultzach to Resinous Products and Chemical Co.

108 U.S.P. 2,228,365 W. Reppe and W. Wolff to General Aniline and Film Co.

109 U.S.P. 2,305,498 E. Segesseman to National Oil Products Co.

110 U.S.P. 1,294,836 K. Schlatter

111 U.S.P. 1,911,722 B. E. Sorenson to E. I. DuPont De Nemours & Co.

112 U.S.P. 2,125,685 O. Nicodemus, H. Lange and O. Horn to I. G. Farbenindustrie

113 U.S.P. 2,279,734 E. E. Dreger, J. Ross and H. G. Kirschenbauer to Colgate-Palmolive-Peet Co.

114 U.S.P. 1,811,959 J. A. Nieuwland to E. I. DePont De Nemours & Co.

115 U.S.P. 1,926,055 J. A. Nieuwland and R. R. Vogt to E. I. DuPont De Nemours & Co.

116 U.S.P. 1,812,541 J. A. Nieuwland to E. I. DuPont De Nemours & Co.

117 U.S.P. 1,812,544 and 1,869,668 A. M. Collins to E. I. DuPont De Nemours & Co.

118 U.S.P. 1,903,501; 1,959,343 and 1,959,408 W. S. Calcott, A. S. Carter and F. B. Downing to E. I. DuPont De Nemours & Co.

119 U.S.P. 2,077,485 W. E. Lawson and J. A. Arvin to E. I. DuPont De Nemours & Co.

120 U.S.P. 2,078,194 A. M. Collins to E. I. DuPont De Nemours & Co.

121 U.S.P. 1,973,493 C. J. Malin and C. R. Fordyce to Eastman Kodak Co.

122 U.S.P. 2,082,797 F. C. Hahn to E. I. DuPont De Nemours & Co.

123 U.S.P. 2,156,144 H. A. Bruson to Rohm and Haas Co.

124 U.S.P. 2,129,722 J. C. Woodhouse to E. I. DuPont De Nemours & Co.

125 U.S.P. 2,166,542 T. F. Bradley to American Cyanamide Co.