as a whole the alkyl sulfates were less irritant than ordinary sodium soaps. In further work dealing with the pharmacology of the fats, fixed oils and their related substances, the cooperation of the oil chemist is not only highly desired but is absolutely essential to success.

Natural and Synthetic Oils in Protective Coatings*

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Introduction:

The production and use of protective coatings stretches so far back into the past that its beginning antedates that of recorded history. There is left to us evidence of usage of such products even by prehistoric cave men. The coatings, then as now, were composed of two essential parts — pigment and binder or vehicle. That the pigments used then are still in use today can be proven. Determination of the nature of the medium used to bind the pigment is more difficult.

However, it can be determined from the records of earliest history that the use of oils of vegetable and animal origin has been known and practiced from the earliest times. Barring most recent progress the art of varnish making as practiced by the ancient Egyptians paralleled very closely in both method and composition of product that of the modern times.

Then, we may safely assume that for countless centuries drying oils have been an essential ingredient in the manufacture of protective coatings. The time of discovery of the two properties of the oils which have made them essential ingredients, viz., the ability to form hard tough dry films when exposed in thin layers to the air and also to become thickened when exposed to heat or sunlight, which thickened or polymerized oils produce smoother and more durable films of higher gloss, lies in the realm of conjecture.

That the property of certain oils to dry and polymerize constitutes the very foundation of the protective coatings industry today is beyond argument. Certainly, the nature and mechanism of these two phenomena known for so long and constituting as they do the corner stone of a vast industry must be very thoroughly understood.

Unfortunately, such is not the case. In spite of the work of numerous investigators, no entirely satisfactory explanation for the mechanism of oil drying or polymerization has yet been advanced. A vast store of empirical information has been accumulated by the protective coatings producer, but fundamental explanations have yet to be made. That considerable progress has been made cannot be denied and practical use has been made of hypotheses advanced. Solution of the fundamental problem will constitute a major step forward, but that step lies in the future. A brief review of some explanations for the phenomena may be of interest.

Drying and Polymerization of Oils:

The ability of an oil to dry is associated with unsaturation of the molecule — measurable by means of the iodine number. Iodine number is not a true measure of drying, but is rather approximate. However, as a general rule, the higher the iodine number, the better drying qualities an oil has.

The drying of an oil appears to involve two types of reactions best described as double bond polymerization and absorption of oxygen. Absorption of oxygen has long been regarded as essential in oil drying. Recently, the theory of "gas coagulation" has been advanced by Auer, but has not received widespread support. The nature of double bond polymerization has been discussed by Cutter and Jordan as a modification of the Diels-Alder reaction, which serves to give a six membered carbon ring linking together two acid radicals of the triglyceride.

Long neglects double bond polymerization entirely and concludes that drying takes place in two stages. The first, the absorption of oxygen to form polar molecules, and second, the association of liquid polar molecules to form a solid insoluble phase. Since we have no means of following molecular weight change beyond the point at which insoluble products are produced, our knowledge of the nature of the insoluble phase is limited.

When a drying oil is polymerized by means of heat, the changes taking place in physical properties are well known. The oil increases in specific gravity and viscosity. The iodine number drops and the acid number rises. The color of the oil becomes darker and there is an increase in molecular weight. The chemical reactions accompanying these physical changes are unexplained. Work in the synthetic resin field has raised some interesting parallels. Once more the diene reaction is thought to play a vital part.

The Drying Oils:

Moving from a field in which speculation plays such a large part onto firmer ground, the constitution of the drying oils is well established. Natural oils which possess the ability to dry are the triglycerides of fatty acids mainly of the linoleic or linolenic series. The natural oils never contain a single fatty acid, but invariably a mixture of acids of varying degrees of unsaturation. That presence of saturated acids in large quantity will reduce the ability of an oil to dry and that presence of a highly unsaturated acid in large quantity will increase its drying power is generally conceded. The individual drying oils of large usage in protective coatings manufacture and their main usage are as follows:

Linseed Oil:

Predominating fatty acids going to make up the ester that is linseed oil are linoleic acid carrying two double bonds and linolenic carrying three double bonds. Approximate percentages are 60% linoleic and 25% linolenic. The remainder is stearic, palmitic, and oleic, all non-drying acids.

Linseed oil is an excellent drying oil and was long the paramount oil for both paint and varnish. It still

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holds this position in the production of house paint. All first quality house paints will have as their binder a major percentage of linseed oil. The oil will be mainly raw oil, but a portion will probably be polymerized to increase gloss, flow and durability of the film.

Until the introduction of tung oil at the turn of the century, linseed oil was paramount in varnish production. Used in conjunction with hard natural resins as kauri, congo, and others, it produced an excellent and durable, but slow drying, varnish. Introduction of tung oil made a radical change in the picture, but with recurrent shortages of tung oil and the introduction of versatile synthetic resins polymerized linseed oil has again assumed greater importance as a varnish oil.

Perilla Oil:

Perilla oil contains as its main fatty acids linoleic and linolenic. Approximate percentages are 38% linoleic and 46% linolenic. With its higher degree of unsaturation, it bodies much more rapidly in the varnish kettle than linseed and dries to much harder films. If used in the raw state in house paint, it has the unpleasant characteristic of causing the film to "crawl" or draw up in droplets rather than forming a smooth film. This characteristic can be overcome by giving the oil a quick heat in the varnish kettle. As a house paint oil, it is important for blending with less expensive and slower drying oils, such as soyabean oil or fish oils.

Its rapid rate of polymerization and fast drying puts it in an intermediate position between linseed and tung oil as a varnish oil. In the past in times of tung oil scarcity, the varnish manufacturer has turned to perilla oil as a tung oil substitute.

Tung Oil:

Tung oil contains approximately 80% eleostearic acid, which has three double bonds, just as does linolenic, with this difference. While the double bonds of linolenic acid are in the isolated position, those in eleostearic acid are in the conjugated position. To this is ascribed the peculiar properties of tung oil.

Whereas hours of heating at high temperatures around 585 to 600° F. are required to gelatinize linseed oil, and a shorter time, still measured in hours, to gelatinize perilla oil, the time required for tung oil to reach a gel at 540° F. is a matter of minutes. This rapid bodying rate which makes possible the rapid and therefore less expensive production of varnish is of tremendous importance to the varnish manufacturer.

Furthermore, the extreme resistance to water and alkali shown by varnishes made from tung oil revolutionized varnish making. It was found that inexpensive rosin in conjunction with tung oil made possible quick production of fast drying varnish of excellent water resistance and good durability. Varnish manufacturers turned from linseed oil and the expensive natural hard resins to tung oil and rosin. When nitrocellulose lacquers began to encroach on sales of oleoresinous products, the varnish manufacturer found that he could compete in the market for rapid drying products using tung oil, and the newly introduced synthetic phenolic resins. Tung oil became the most desirable varnish oil. Periods of shortage of tung oil, and skyrocketing prices therefor, soon convinced the user that it was to his advantage to limit his dependence on this material. Progress in the development of synthetic resinous materials permitted him to increase his usage of linseed and perilla oil with no sacrifice of drying speed, water or alkali resistance and with some increase in durability of his product. Further crises in supply led the users to believe it was to their advantage to reduce the use of the oil further and he prepared to dispense with its use altogether, if necessary. Hence, for years there has been a search for a natural oil to replace tung oil or a means of preparing a substitute from natural oils at hand. Of that, more will be said later.

Tung oil, in its raw state, dries to a frosted, wrinkled film. For this reason, uncooked tung oil has found no place as a house paint oil. After cooking it finds a relatively small usage in house paints for reinforcing the drying of the slower drying oils.

Oiticica Oil:

The search for an oil to replace tung oil in varnish manufacture led to the discovery of oiticica oil, a product of Brazil. The supply offered so far has been somewhat small, but is constantly on the increase. The fatty acid to which oiticica oil owes its properties is licanic, which has three double bonds in conjugated position, but also carries a carbonyl group in the chain. The oil bodies and dries somewhat more slowly than tung oil and in combination with certain resins to much more brittle films. The oil foams badly in the kettle with limed rosin. However, if the proper resin is chosen, varnishes can be made which surpass a similar tung oil varnish in speed of dry and durability.

Fish Oils:

When first introduced, fish oils were non-uniform, malodorous, poor drying materials and an unfortunate prejudice grew up against them in the paint and varnish industry. More efficient methods of processing and treatment have been developed and certain fish oils have very desirable properties which make them valuable paint and varnish ingredients. The elasticity of the film and excellent solubility and stability of the oxidized oil are worthy of mention.

Fish oil dries to a somewhat tacky film, which tack disappears slowly and thus when used in house paint, must be compensated for by blending with a better drying oil as perilla or polymerized tung oil.

The refined oil may be bodied in the kettle at the usual temperature and finds wide usage as a varnish oil.

Other Oils:

Linseed, perilla, tung, and fish oils constitute the oils used in the largest volume in the manufacture of protective coatings. However, there are many others. Of great interest is soyabean oil. Due to the high oleic acid content of the oil, approximately one-third of the total, the oil dries slowly to a somewhat soft film and bodies very slowly in the kettle. However, in combination with other better drying oils, for example, perilla, the raw oil may be used as a house paint vehicle most successfully. A combination of 70% soyabean and 30% perilla oil gives an excellent account of itself with respect to exterior durability in house paint.

Kettled in combination with other oils or blown, the oil is widely used in interior finishes and is valued for the non-yellowing film it produces.

Other oils of limited usage due to small and uncertain supply are hempseed, safflower, sunflower seed, walnut, poppy seed oils and others. All have specific properties which make them valuable for certain uses.

Alkyd Resins:

Alkyd resins, composed of esters of glycerin with dibasic acids as phthalic, succinic, maleic and others, modified with drying oils may be considered as combining oil and resin within the same molecule. It is not possible to make a finished ester of glycerin and phthalic anhydride and use this resin with drying oil in producing a varnish, as it the case with phenolic resins for example.

In the production of these materials, either the fatty acid of the oil is used to complete the esterification of the partially formed phthalic glyceride or a monoglyceride of the oil is formed and esterification completed with the dibasic acid.

The properties of the resin are governed by the nature and quantity of drying oil used in their modification. The general characteristics of the oil are carried over into the resin. Thus, all of the oils mentioned have a place and usage in the manufacture of alkyd resins.

Source of Drying Oils:

The United States is in a most unfortunate position with regards to a domestic supply of drying oils. Almost all of the oils used in the production of protective coatings are imported. Flaxseed is a domestic crop. Nevertheless, approximately half of the flaxseed from which linseed oil is produced is imported into this country. Perilla oil is produced in Manchukuo. None is produced domestically. Oiticica is produced exclusively in Brazil.

Soyabean oil is of domestic production and the supply is constantly increasing. It is to this oil that the attention of the paint and varnish manufacturer is turning. It is safe to say that the importance of this oil will show considerable increase in the manufacture of protective coatings. The problem is not easy and there are many difficulties to overcome, but the problem is far from insoluble.

Tung oil, occupying the peculiar position that it does, is of major interest. A campaign to produce tung oil in the United States, in the geographic locations which are suitable, has been underway for some years and the domestic supply is constantly on the increase. However, the importations of tung oil in 1937 were 175,000,000 lbs. Domestic production last year was 4,000,000 lbs. Thus, we see that domestic self sufficiency is far in the future.

The disturbed conditions in the Orient have drastically curtailed supply of tung oil. Supplies have dwindled and prices have skyrocketed. It has been already said that to a limited degree the various drying oils may be substituted for each other in paint and varnish formulation, but the supplies of other drying oils are not sufficient to compensate for drastic curtailment of the tung oil supply. Recently, oiticica has disappeared from the market and prices for perilla and linseed have risen somewhat violently in sympathy with tung oil.

The solution to the problem is clear. A new material is badly needed to take the place of tung oil, both from standpoint of stabilizing the market and maintaining a reliable source of supply of raw material. To that end the producer of protective coatings has turned his attention to synthetic oils with the properties of tung oil. Efforts have been successful.

Synthetic Oils:

Recently, it has been found commercially practical to separate by fractional distillation under vacuum the fatty acids contained in fish oils. A fraction having a very high iodine number, approximately 225-250, is obtainable which on esterification with glycerine produces an oil which bodies rapidly in the varnish kettle and dries rapidly to hard tack-free films. Unfortunately, there are some disadvantages. The films lose their elasticity rapidly and become quite brittle. The water and alkali resistance of the films are on the order of those produced from perilla oil and are inferior to tung oil films. Offered at a competitive price, these oils have found acceptance as a paint and varnish ingredient and should rise in volume rapidly, especially under the condition in which the drying oil market finds itself today. The oils are particularly important since fish oil, their source, is of domestic origin.

Dehydrated Castor Oil:

Castor oil is a potential rather than an actual domestic product. In contrast with tung trees which can be grown in only limited areas and need a number of years to reach the bearing stage the castor plant is an annual which may be grown in widespread parts of the country. It has been shown that if all the byproducts of the production of castor oil are used, namely, the stalks of the plant for cellulose production, the press cake for fertilizer, that castor oil can be a commercially profitable crop in the United States. Although most of the present supply comes from Brazil, since there is the possibility of obtaining economic self-sufficiency either wholly or in part, the oil is of decided interest.

Castor oil, having an iodine value of less than 90, is a non-drying oil. However, the fatty acid which makes up a major portion of the oil, ricinoleic acid, is unusual in that it carries a hydroxy group on the chain.

The discovery that castor oil could be converted into a drying oil was made quite by accident, we are told. Efforts which led to the discovery, made about 1898, were directed toward using castor as a lubricating oil in blends with mineral oils with which the natural oil is not miscible. It was discovered that on heating the castor and mineral oils become miscible and furthermore, that the castor oil after heating had the properties of a drying oil.

A drying oil produced by simply heating castor oil was patented in Germany in 1904. Such an oil made its appearance on the market, but was not highly successful. The first successful method for the production of a drying oil from castor was by the Scheiber process. The oil originally known as Scheiber oil is now sold under the name of "Synourin." The process consists in the dehydration of the fatty acids derived from castor oil by heating under reduced pressure at 200° C. with or without catalysts as alumina or silica gel, producing linoleic acids, mainly of the conjugated isomeride type which are then re-esterified with glycerol or other suitable polyhydric alcohols.

The reaction may be represented as follows:

$$CH_3\ (CH_2)_5\ CHOH.CH_2.CH = CH\ (CH_2)_7.COOH$$

Ricinoleic acid →

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

9:11 conjugated linoleic acid +

$$CH_3(CH_2)_4.CH{=}CH_2CH\ \ CH{=}CH.(CH_2)_7\ COOH$$

9:12 isolated linoleic acid

The 9:11 conjugated linoleic acid represents the ideal product, which product is never 100% obtained.

A percentage of the isolated acid is obtained and the main reaction is accompanied by side reactions producing undesirable decomposition products.

This process, involving preparation of the fatty acid, its dehydration and subsequent esterification is naturally quite expensive. Work by other investigators has shown that dehydration of the castor oil fatty acid does not necessarily have to be carried out on the fatty acid in a free state, but also on the triglyceride itself. A host of catalysts have been patented for the process, generally of an acidic nature and varying widely in efficiency. However, by the most refined of the modern processes, it has become possible to produce a completely dehydrated castor oil which is free from objectionable decomposition products.

The oil is of great interest for two reasons. First, because of the value of the product.

Carrying as it does two conjugated double bonds in the fatty acid molecule the properties of dehydrated castor oil as it comes to the market today begin to approach those of tung oil for which a substitute has so long been sought. The oil bodies with great rapidity in the varnish kettle. Varnishes prepared from it dry rapidly to hard tough and elastic films which have marked resistance to hot and cold water and alkali solutions. As received the oil dries to a frosted wrinkled film just as tung oil does. That the oil is not identical with tung oil is evident. The fatty acid of tung oil carries three double bonds in comparison with only two for the dehydrated castor oil. The difference in behavior of the two oils is in approximately the same ratio in some respects.

Dehydrated castor oil is a welcome new ingredient to the manufacturer of protective coatings since, while not a direct substitute for tung oil, he is able by its use to replace tung oil in his formulas with less change in the formula than is necessary with any of the other substitute oil which have been offered. A main point of difference between varnishes prepared from tung oils and dehydrated castor oil is the greater softness of film of the dehydrated castor oil varnish. This difference is easily compensated for by the addition of harder resin, preferably synthetic phenolic resin for greater speed of drying.

In much the same manner that tung oil is used to speed drying and to form a firmer film in blends with the slower drying oils dehydrated castor may be used for the same purpose, except that a larger quantity of the castor will be necessary to obtain the same result.

The second point of interest is that the development and use of dehydrated castor oil represents an important step forward in a new field. The product represents an entirely new drying oil not found in nature, but produced by alteration of the structure of a fatty acid molecule by chemical reaction.

The attention being given to the first synthetic oil mentioned and to dehydrated castor oil signifies that the manufacturer of protective coatings is no longer content to accept as the ultimate, oils supplied by nature and to limit himself to the effects he can produce with natural oils. For a long time he has compromised on the undesirable features of the natural drying oils overcoming the shortcomings of one by blending with another. The viewpoint is changing. He now looks for methods whereby he may produce oils of the desired properties by synthesis of the oil molecule and even alteration of the fatty acid itself. This viewpoint opens up the possibility of producing synthetic oils formulated just as is a paint or varnish to serve a specific purpose.

It seems safe to say that in the future more and better synthetic drying oils will make their appearance in the protective coatings industry and that these synthetic oils will surpass in performance the drying oils supplied by nature.

Industrial Utilization of Tall Oil*

by ARTHUR POLLAK

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ABOUT fifteen years ago a confidential questionnaire was circulated among American pulp and paper manufacturers questioning them on the best means for disposing of a troublesome, frothy paste that seemed to settle out of pulp mill waste liquors, plugging pipe lines and clogging equipment. The response concurred remarkably in the opinion that (1) the material was a nuisance, (2) the best way to be rid of it was to burn it up.

Tall oil is derived from these waste liquors of the paper and pulp industry. As first recovered it appears as a brown, frothy paste. When properly treated, it may be consolidated to a more or less homogeneous phase consisting of the sodium soap of tall oil, associated with about 35% of water. This soap may be spray dried or vacuum dried to a powder. The original paste or the consolidated soap may be treated with acids to give crude tall oil. Such crude tall oil may be subjected to one of several refining processes to improve its color or its odor or to separate various constituents.

Most of these processes were first developed in Europe, especially in the Scandinavian countries, where talloel, or tallöl, as it is known there, has been produced since the beginning of this century.

In 1930, when first produced in this country, tall oil was ranked as a fatty acid. Resembling commercial red oil in many of its properties, it was first offered as a substitute for it. Later, as its properties became better known, new uses for tall oil developed. At the present time its most effective advantage for most large users is its extremely low price. Crude tall oil is cheaper than any other organic acid available. Thus in December 1939, the price, in bulk, F. O. B. works, was being quoted at 30 dollars per ton. Tall oil has become well established commercially and merits the serious attention of potential users. The origin, the principal forms, and the properties of tall oil have already been described on previous occasions. Methods for the analysis of tall oil have also been described.

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