CHINA WOOD OIL

By MAXIMILIAN TOCH

The article that follows appears as a chapter in the third and most recent edition of a book by the author, entitled Chemistry and Technology of Paints. The paper deserves to rank as the most complete, up-to-date and authoritative discussion of China Wood Oil that has been published. To quote Dr. Toch: "Our viewpoint on China Wood Oil has been largely changed, due primarily to investigations of the growth of the tung oil tree and the collection and expression of the seeds, and for the further reason that the transplantation of the tung oil tree on a large scale in the United States has given us an oil which differs materially from that which we have considered standard China Wood Oil." The importance of the work, specially as it affects the paint industry, is such that we have secured permission to reprint part of the chapter from the author and from the publishers, D. Nostrand & Company, New York.—*THE EDITOR.*

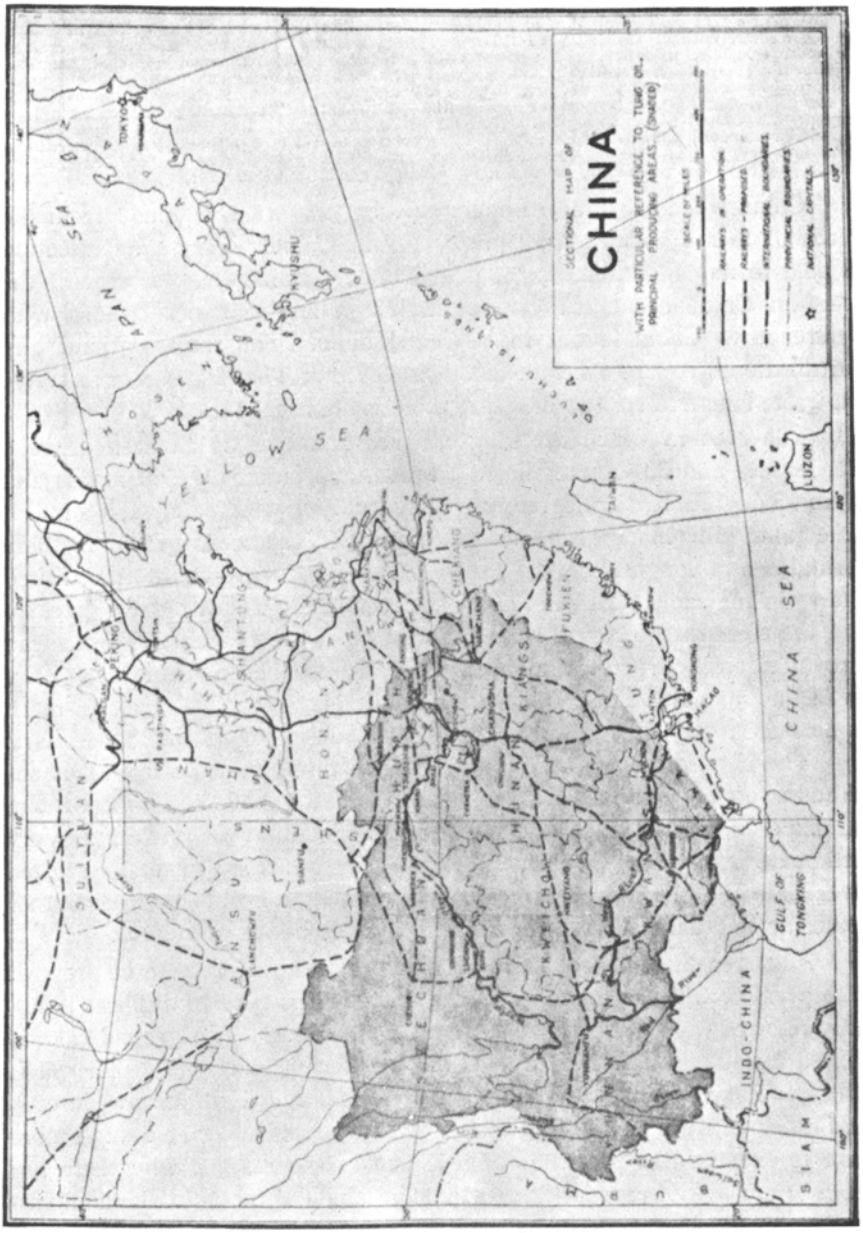
China wood oil is also known as tung oil. It is obtained from the seeds of a tree which grows principally in China. Very little attention is paid to its cultivation, and it is estimated that not five per cent of the trees in China are taken care of, although any statistical record with reference to China is not to be relied upon. The trees, without any fertilization, grow to a height of 30 to 40 feet. They also seem to thrive on waste land and rocky soil where there is sufficient rain.

The area in which the tung oil tree flourishes is an area between 23 degrees and 33 degrees north latitude, approximately 600 miles; and from 95 degrees to 115 degrees west longitude, approximately 1,200 miles. The same indigenous difference takes place in the seeds grown in these latitudes and longitudes that there is in tobacco grown in the United States in the same relative area. The trees in the South mature quicker, but the trees in the North are hardier, so that the Hupeh and Szechwan provinces really produce the finest grade of oil. The tung oil tree grows in fact as far north as Shanghai where there is snow and ice, so that there is no reason why the tree cannot be planted where they have cold winters.

The nuts, produced by the tree, contain three, four, or five seeds enclosed in a very dense shell. I have seen nuts that have been worm-eaten, decomposed, and in an otherwise unsuitable condition for pressing. Very little care is exercised in their selection. The seeds are generally roasted over fires to split the outer shell, and whether they are over-heated or under-heated makes very little difference to the native producers.

After roasting, the seeds are ground and are then ready to be pressed. The presses, which are similar to the antediluvian type of Biblical times, are hollowed out of the trunks of hard wood trees. The ground cake is placed inside and the oil is pressed out by driving in wedges. The oil is collected in wicker baskets that are paper-lined, and dead animals, insects, and other offal frequently find their way into these baskets, although more care is exercised at present. This is one of the reasons why there has been so much difference in the constants of China wood oil. The adulteration with other oil also made a great difference in the material that has been shipped to foreign countries.

The actual chemical composition of China wood oil will probably be



Black Area Shows Tung Oil Region

established with more certainty than it is at present, when a standard shall have been made of oil, which is expressed with modern machinery or extracted with solvents, from selected nuts grown on fertilized soil. But suffice it to say that China wood oil consists principally of elaeomargarine, also known as elaeostearine.

Much of the literature of China wood oil is hearsay, as, for instance, the statement that the Chinese have used it for thousands of years on junks and other woodwork in its raw state. It is probably true that for many centuries this has been the principal oil for varnishing or waterproofing paper, such as umbrellas, the backs and sides and masts of the junks, and wooden floors of compounds. On the finer class of river craft, and on table tops and inlaid furniture I found that Ningpo lacquer, and a mixture of lacquer and China wood oil, was used.

Another myth that has appeared from time to time, is that Hankow oil is the only good oil produced in China, and Canton oil is no good. As a matter of fact, there is no such thing as Canton, Hankow or Hongkong oil. These cities are simply collecting points, and one might just as well speak of Liverpool, Buffalo or Duluth linseed oil.

The importance of China wood oil in the paint and varnish industry may be simply expressed by the fact that in 1896 a few barrels were exported, whereas in 1924 fifteen million dollars' worth was exported.

The Chinese merchant is no different from the merchant of any other country in so far as he will adulterate any product with a cheaper material in order to make additional profit. This has led the Chinese to use any oil which is cheaper than China wood oil, and at this writing mineral oil or paraffine oil is used. This adulterant is about one-third the price of China wood oil, and somewhere between the pressing of the nuts up the Yang-tse River and the delivery of the oil to Hankow or Canton other oils have been added in the nature of adulterants and this has done the industry and the manufacturers a great deal of harm.

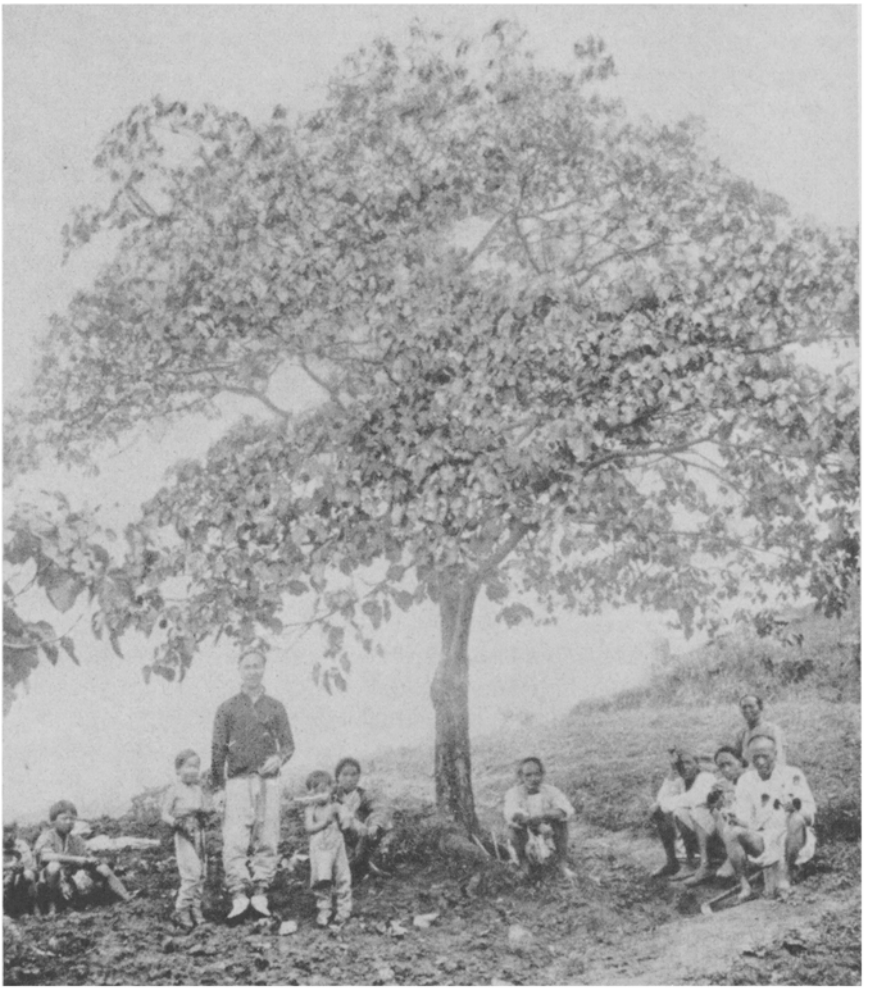
For years many chemists have been at work standardizing China wood oil, and given ample time, it is quite possible to determine the purity of any shipment of China wood oil within reasonable limits.

The average constants of China wood oil known to be pure all indicate that the oil must have a gravity of at least .940 at 15.5 degrees C., but China wood oil can be pure and have a specific gravity of .938. The iodine value will range between 159 and 167, the saponification 190, and the acid value from one to seven.

A great many determinations of the constants of China wood oil of known origin and direct importation were made, as will be seen in the following pages. An investigation on the examination of the same types of oil mixed with 5, 10 and 15 per cent of other oils has also been tried.

It is worthy of note that the heat test alone as indicated in some of these samples is not significant, and varnishes made with China wood oil adulterated with 5 per cent of many oils do not give any immediate indication of admixtures. The variation in acid number is a factor in polymerization. The higher the acid number, the longer the oil takes to polymerize.

However, from the business standpoint no manufacturer wants to buy an oil which is impure, and the tests up to the present writing permit the acceptance of oils that are not pure. The object, however, of this lengthy and careful investigation is to establish a method which shall be quick and

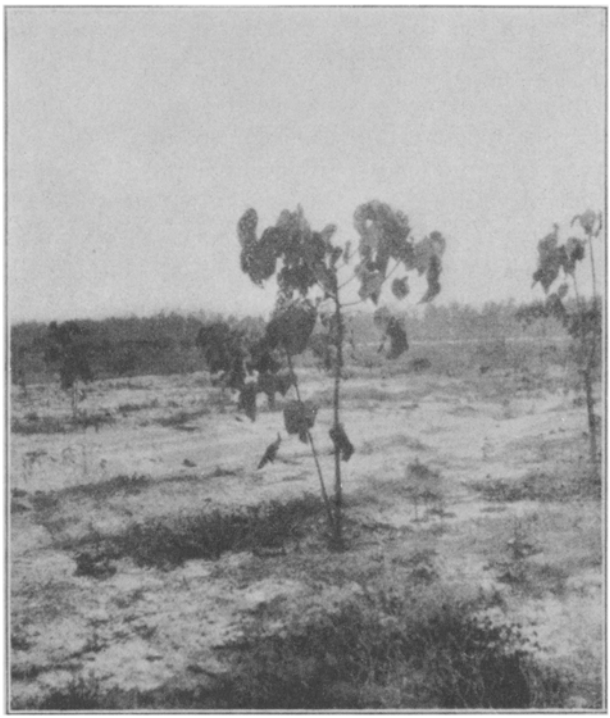


The Tung Oil Tree in China

accurate, and which will indicate beyond peradventure that the China wood oil examined is pure or impure. As every one in factory practice knows, when a shipment of material is delivered, the cost of taking it into the warehouse and putting it in tanks while it is being analyzed involves labor and expense which is part of the business organization if the material is accepted, but if the material is impure and has to be pumped out of tanks and re-filled into barrels or other containers and shipped back again to the consignee, it adds undue expenses which may or may not be refunded.

It is for that purpose that I am establishing the following methods for the testing of China wood oil which are quick and absolutely correct. After these tests have been made, should further tests be desired, such as saponification, acid number, iodine number, polymerization, etc., they can be done at leisure, but these tests take a long time, and can only be used to establish, ratify and corroborate any previous decision.

It is perfectly possible to adulterate China wood oil with 5 per cent paraffin oil so that it will pass the polymerization test, and have the accepted specific gravity, but it is very simple to detect the admixture of an oil of this kind even though the gravity and polymerization are correct if the refractive index and color dispersion are made.



American Tung Oil Tree, Two Years Old

Specific gravity, color dispersion, and refractive index occupy only a few minutes, and when these three constants agree with the established standard for pure oil, it is absolutely positive that all the other constants will be in harmony.

Referring again to the case of the adulteration of China wood oil with paraffin oil,[1] and where the saponification test is made, it is easy enough to extract paraffin oil, because it will not saponify. When 5 per cent of any oil is added to China wood oil, one of the two indicators, that is, either refractive index, or color dispersion, will be thrown out of standard, and up to now no sample of adulterated oil which we have examined gives concordant figures for all three of the indicators which I propose.

The best instrument of the kind is the Abbé type of refractometer.

There is only one wood oil refinery in China. This is owned by a Chinese corporation at whose head there is an English chemist. All the others are warehouses and oil storage plants where the oil is received in baskets, strained and placed in tanks where it is heated up to about 105° C. and allowed to set anywhere from one week to a month or more, depending entirely upon commercial conditions.

The foots or sediment are returned to the original Chinese shippers and not paid for, and this oil finds a ready market among the Chinese for waterproofing various fabrics and for the varnishing of junks.

The Chinese are exceedingly apt in heating tung oil in little earthenware dishes at low temperatures, principally not over 125° C., and it is kept at this temperature until the oil thickens slightly. It is then applied by means of either a stiff brush or rubbed on the wooden surface of the junk and scraped off. In this manner many coats are applied.

For the varnishing of floors, in China in some of the private houses, called compounds, the floors are most beautifully polished. A small amount of Ningpo Varnish is added to the wood oil.

The Refining of Crude China Wood Oil

Crude China wood oil is turbid and has a yellow color and a characteristic odor. The two samples of crude oil taken for this investigation were received direct from Hankow. They show the following constants:

1.	Specific Gravity (60° F.)	0.9399
	Refractive Index (21.5° C.)	1.5176
	Dispersion Value (21.5° C.)	0.02025
	Heat Test (Browne's)	11¼ min.

[1]This was first worked out under the name of the Potsdamer method, in the laboratory of Toch Brothers, Inc., Long Island City, more than thirteen years ago. See "A Method for the Detection of Adulteration of China Wood Oils." L. S. Potsdamer. Eighth International Congress of Applied Chemistry. Sec. Ve. 1912

2.	Specific Gravity (60° F.)	0.9408
	Refractive Index (21.5° C.)	1.5176
	Dispersion Value (21.5° C.))	0.02032
	Heat Test (Browne's)	11 min.

Three general processes of refining the crude oil were tried in the laboratory: (1) Heating. (2) Oxidation. (3) Absorption.

The procedure for each experiment was varied in order to find out under what conditions the best result could be obtained. However, in each case two hundred grams of oil were treated in a beaker having a capacity of 400 c.c. The exact manipulation and the effect of such treatment upon the constants of the original oil will now be described carefully: [from (a) to (d) refer to crude oil No. 1; and (e) and (f) refer to crude oil No. 2].

(a) 1 per cent of barium peroxide, mixed with 50 c.c. of water, was added to the crude oil. The mixture was then heated up to 90° C., when dilute sulphuric acid was added drop by drop to evolve the oxygen from the barium peroxide. The oil, after such treatment, was poured into another beaker. One per cent of powdered pumice and 1 per cent of Fuller's earth were then added. The mixture was again heated to 105° C. and agitated for 30 minutes. The oil was not clear after filtration and on further standing the white precipitate increased. Upon examination, it had the following constants:

Specific Gravity (60° F.)	0.9399
Refractive Index (21.5° C.)	1.5177
Dispersion Value (21.5° C.)	0.02039
Heat Test (Browne's)	10½ min.

Whenever crude China wood oil is treated with barium peroxide, the oil is bleached; but it does not remain clear on standing. This is probably due to formation of an insoluble barium compound, resulting from the chemical reaction between barium peroxide and the oil.

Flashing is liable to take place when barium peroxide, without the addition of water, is heated up with the oil. This can be avoided by first bringing the oil up to a high temperature, and then dropping in the barium peroxide.

(b) The oil was treated with 2.5 per cent of an activated carbon. The mixture was heated up to 105° C. and stirred for half an hour. After filtration, the oil was clear and bleached to a certain extent. The constants of this oil were:

Specific Gravity (60° F.)	0.9405
Refractive Index (21.5° C.)	1.5178
Dispersion Value (21.5° C.)	0.02048
Heat Test (Browne's)	10½ min.

A peculiar chemical action was observed—that the oil which was treated with an activated carbon began to crystallize in four or five days and finally turned entirely into a solid white mass. The acid numbers of this oil and of the original oil are practically the same, being 8.6 and 8.75 respectively. The melting point of the solidified tung oil is between 51° and 53° C. This solid form is probably the glyceride of B-Elaeostearic acid, formed by a molecular rearrangement of the liquid form and which is catalized by activated carbon. It was first noticed by Cloez that light has the same effect of changing liquid tung oil into the solid form.

(c) The crude oil was simply heated up to 200° C. and the temperature maintained for ten minutes and finally filtered. The oil obtained has the following constants:

Specific Gravity (60° F.)	0.9420
Refractive Index (21.5° C.)	1.5170
Dispersion Value (21.5° C.	0.02000
Heat Test (Browne's)	10½ min.

(d) The crude oil was mixed with 5 per cent of Fuller's earth and heated to 150° C. for fifteen minutes with constant stirring. After filtration, a very light colored clear oil was obtained. The oil also remains in good condition on standing. Its constants may be shown in the following table:

Specific Gravity (60° F.)	0.9401
Refractive Index (21.5° C.)	1.5179
Dispersion Value (21.5° C.)	0.02053
Heat Test (Browne's)	10½ min.

(e) For thirty minutes the crude oil was heated up to 120° C. with 1 per cent bone black. Then it was filtered. The oil was clear and bleached to some extent. It had the following constants:

Specific Gravity (60° F.)	0.9397
Refractive Index (21.5° C.)	1.5176
Dispersion Value (21.5° C.)	0.02043
Heat Test (Browne's)	10½ min.

(f) The crude oil was treated with 2 per cent of Fuller's earth and 2 per cent of bone black. The mixture was heated up to 120° C. for thirty minutes and then filtered. The oil obtained was very pale in color and clear. It had the following constants:

Specific Gravity (60° F.)	0.9395
Refractive Index (21.5° C.)	1.5175
Dispersion Value (21.5° C.)	0.02042
Heat Test (Browne's)	10½ min.

Many other methods have also been tried in the laboratory such as the use of the oxygen liberated from manganese dioxide, potassium bichromate, and sodium peroxide. Bleaching with sulphur dioxide and chlorine gas did not give any striking effect. Among all the methods tried bleaching with 5 per cent Fuller's earth, or with a combination of Fuller's earth and bone black, gave the best result.

(To be concluded in February)