Heat Bodying of Drying Oils

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DRYING oils have been heat bodied to improve their characteristics for many years. With the conjugated oils, particularly with tung and oiticica oils and to some extent with dehydrated castor oil, bodying is essential to give vehicles which do not wrinkle on drying. Also heat bodying occurs when oils are heated in the varnish kettle to incorporate resins. It is recognized that heat bodying imparts many desirable properties to all of the drying oils.


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While bodying has been practiced for many years, our knowledge of the chemistry of the process is still incomplete as evidenced by the lack of complete agreement on the mechanism of some of the essential steps. Part of this lack is perhaps due to a reluctance to investigate a process that has been so thoroughly studied empirically, with only a slight hope of arriving at any pronounced improvement. Also the chemistry of the process is surprisingly involved for a reaction which appears relatively simple. Recent work has greatly clarified the mechanism of the reaction, but it can hardly be said to have simplified it. There still remain many problems in this field to challenge the ingenuity of the most imaginative investigator.

Heat bodying is usually carried out in metal kettles; copper, monel, and stainless steel have been used. Smaller batches are often bodied in open kettles over a direct fire. Modern practice tends to larger closed kettles which may be heated electrically or by circulating hot oil or Dowtherm. Many of these kettles are mechanically agitated to insure more uniform heating. An inert atmosphere is often introduced to protect the oil from discoloration by access to air.

Bodying is usually carried out at temperatures between 450 and 625°F. (232 to 330°C.). Conjugated oils body quite rapidly, and the lower temperature ranges are employed while linseed and soy are much less active and require the higher temperatures. Frequently heating is started at a relatively high temperature and finished at a somewhat lower temperature to have more latitude when the desired viscosity is approached. Accurate temperature control is desirable, but the end point is often taken when the desired viscosity is attained.

Structure of the Drying Oils

The behavior of a bodied oil might naturally be expected to be quite dependent on the arrangement of the fatty acid groups in the glyceride structure of the oil. Thus an oil consisting of one-third stearic acid which is unaffected in heat bodying and two-thirds of an active unsaturated acid, linolenic for example, might have several arrangements. First, the oil might consist of only tristearin and trilinolenin, or it might consist only of monostearyldilinolenin. Finally, it might consist of the above esters and distearylmonolinolenin, arranged in an entirely random fashion.

Much study has been made to determine the arrangement of the acid groups in the natural oils. It is not entirely clear what the arrangement is in many cases. A recent careful study of soy (9) oil indicates that it may possibly be entirely random, and other studies, particularly of vegetable oils, have indicated considerable regular arrangement as in the case of the single glyceride cited above. However when heat bodying is carried out at the temperatures usually employed, the arrangement of the glycerides is a matter of little consequence. Ester interchange occurs readily under the conditions of heat bodying, and the glycerides soon assume a random arrangement. Even when two different oils are bodied together, the acid groups rearrange between the two oils, and the mixture behaves (2) as if it were a single oil made up by random arrangement of the acids of the two oils in the glyceride structure.

If the oils were oriented and remained so under bodying conditions, much greater activity might be expected. Also the removal of unreactive portions of the fatty esters by refrigeration of solvent extraction of the oils would be a much simpler operation.

Polymerization Reactions

Isomerization. The 1,4-di- and 1,4,7-triunsaturated acids which are present in linseed, soy, dehydrated castor, corn, and other drying oils apparently do not combine with similar fatty acid groups. The conjugated or 1,3-dienoic structure must be present before such combination can occur. Thus the oils which do possess the conjugated structure body much more readily since they are already in a reactive form.

At the temperature of heat bodying the double bonds migrate and conjugated dienes are formed. The bonds can migrate in either direction, from or toward the next double bond. If they migrate to form a 1,5-diene, it is apparent that this form cannot be active in combining with another unsaturated acid group. When three double bonds are present, as in linolenic acid, it will be seen that the probability of forming a conjugated structure is much greater. This may, in part, explain the considerably greater activity of linolenic acid as compared to linoleic acid.

It has been found that some dienoic acids are formed in heat bodying which are not reactive. These (13) are the 1,5-dienoic esters which cannot readily isomerize to a conjugated form.

Ring Formation. Conjugated dienes add readily to active double bonds at ordinary temperatures to form a six-membered ring containing one double bond. At heat-bodying temperatures, conjugated dienes combine (4) with double bonds to form a ring. Apparently oleic esters can combine in this manner although not so readily as more unsaturated fatty acid groups (2, 12). 9,12-Linoleic esters combine with conjugated dienes, but conjugated dienes add to each other much more readily. Still faster reactions have been noted when trans-conjugated structures add. This ring formation leads to a bond between two glycerides and results in formation of bigger molecules as more and more glycerides combine. The increase in viscosity is a result of this polymerization.

While the dienoic acids add to form a dimer containing a single ring, it appears that the addition products form triunsaturated groups, which may, to some extent, go farther and form a structure containing (3) two rings. The iodine value and other physical properties suggest such a structure. However the second ring adds nothing to the polymeric structure of the oil.

It has been found that a third fatty acid group can combine, and a conjugated group can add to one of the groups already combined to form a second ring (3). This reaction apparently is a subsequent step to the first ring formation for more of this trimer is found at later stages of the heating (13) (Figure 1).

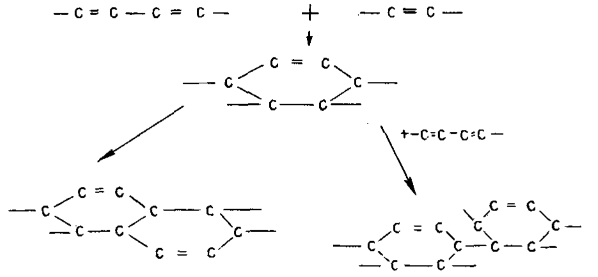

Fig. 1. Ring structures.

Although ring formation does lead to bonds between glycerides, this is not always the case. A conjugated triene can form a ring without adding to another molecule. Such a ring does not add to the complexity of the structure nor does it increase the viscosity. Links between groups which form large closed rings in the chain structure are also ineffective in the polymerization. It is possible that two fatty acid groups in the same glyceride may so combine (1). Such bonds may become effective when one of the groups undergoes ester interchange with another glyceride molecule, as illustrated in Figure 2. Structures of this type have been designated as intrapolymers since combination is within one molecule.

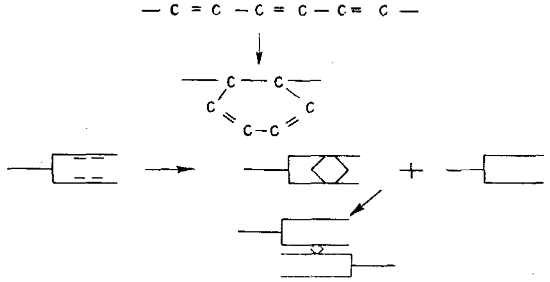

Fig. 2. Intrapolymers.

Polymerization of Glycerides

So far, chiefly the addition of fat ester groups and the conditions of their combination have been considered. The glyceride structure of the oils, each containing three locations at which addition may occur, introduces the possibility of forming some very complex structures or, in other words, some very large molecules. The complexity increases if all three of the groups in the glyceride are reactive.

If only one group in the glyceride is reactive, it can add to another such glyceride, and less probably, a third molecule can add (Fig. 3). This would not result in any great increase in viscosity.

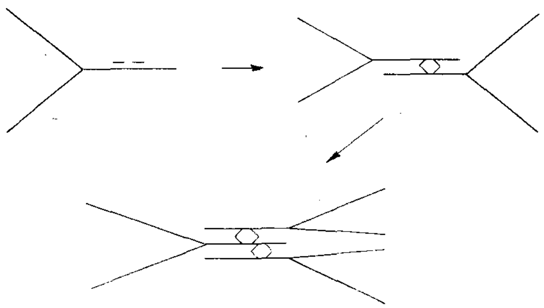

Fig. 3. Monoreactive glycerides.

If however two of the three groups can enter into combination, it can be seen that much larger structures can be formed. As each group adds to another glyceride, a chain molecule is formed. This could proceed to form highly viscous oils (Figure 4). The glycol esters of the dimer of linoleic acid have a similar structure (8), and very viscous esters have been so produced. However most natural oils contain monounsaturated materials which end the chain and reduce the size of the possible structure. It is however possible that a certain number of groups may add to the bonds already formed. These would give branches and cross links which, if carried far enough, would form exceedingly large molecules. This condition is evidenced by the formation of a gel, an insoluble and infusible mass. This can occur with reactive oils and results in an unusable, insoluble material if the bodying is allowed to proceed too far.

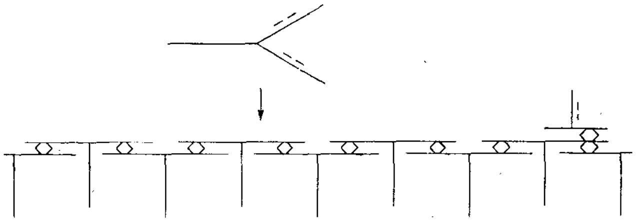

Fig. 4. Direactive glycerides.

When trireactive glycerides combine (Figure 5), it can be seen that the structure grows in three directions, and even though only one bond is formed between the reactive groups, very large molecules are formed as combination between the reactive groups proceeds. With such reactive materials it is essential to stop the bodying before a highly cross-linked, unusable mass is formed.

Most commercial oils contain unreactive, monoreactive, direactive, and trireactive glycerides. It can be shown that, unless two-thirds of the acids in an oil are reactive, it will not be useful as a drying oil. This has been represented by the direactive glyceride above for which considerable activity was predicted;

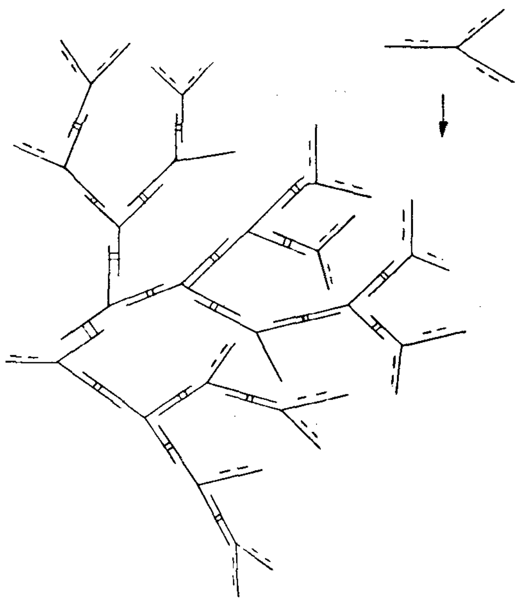

FIG. 5. Trireactive glycerides.

as will be seen, various acid groups vary greatly in activity; even oleate esters, once considered entirely inert, do combine to a small extent in the bodying reaction. Conjugated groups are more reactive than unconjugated, and reactivity is greater with increase in unsaturation. Since tung oil contains a high percentage of a conjugated triunsaturated acid, it is the most active of drying oils in the varnish kettle.

Gel Formation. We have seen that formation of cross links from glycerides with a high reactivity can lead to formation of insoluble materials. In commercial practice this would be an undesirable result since the final product is unusable. Careful control of temperature and conditions of bodying is used to prevent overbodying. Also varnish resins, many of which are acids which do not polymerize further, may be interchanged into the glyceride structure and reduce its complexity.

Viscosity of Heat-Bodied Oils

Many of the properties of drying oils change as they are heated; the density increases, the refractive index of conjugated oil decreases and in the case of unconjugated oils increases, but the most apparent change is the increase in viscosity. As the temperature is increased, viscosity increase is faster, and the rate of bodying doubles (16) with an increase of 12-14°C. in the temperature of heating.

It is often found that plotting of viscosity against time gives a curve which turns up abruptly as higher viscosities are reached. When however the logarithm of viscosity is plotted against time, a linear plot is usually obtained. Careful study has shown that this curve (2) may consist of three regions, each of which is nearly straight but differs only slightly in slope from each of the others. It is usually found that there is a tendency for the curve to turn up as high viscosities are reached. However the curve is nearly linear over most of its length so that its slope may be taken as a measure of the rate of bodying of an oil at any temperature. Curves showing the viscosity increase on linseed oil, dehydrated castor oil, tung oil, and oiticica oil, at several temperatures, are shown in Figures 6, 7, and 8.

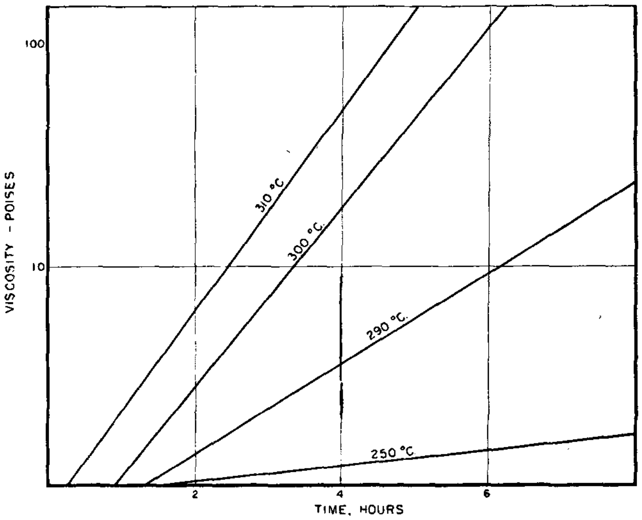

FIG. 6. Bodying of linseed oil (7).

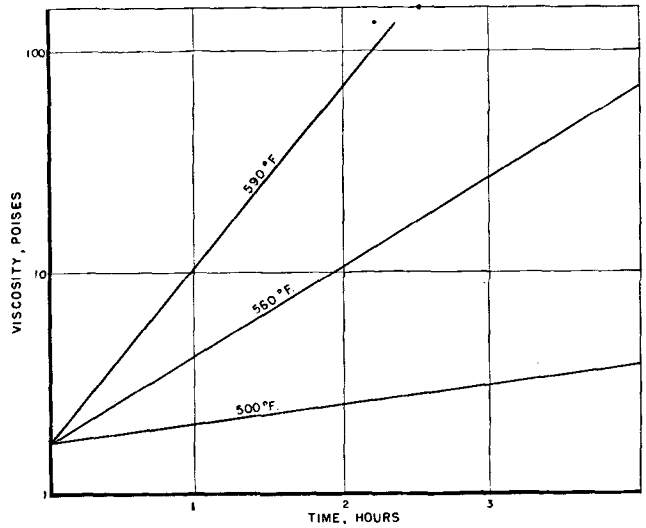

FIG. 7. Bodying of dehydrated castor oil (16).

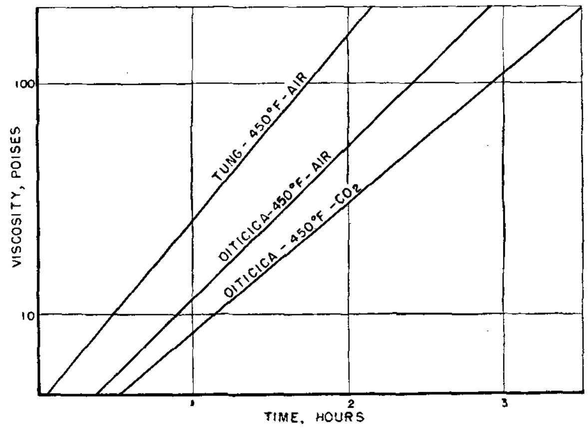

FIG. 8. Bodying of tung and oiticica oil (15).

The bodying constant is measured by the slope of these curves where

$$K = (\text{Log } v_2 - \text{Log } v_1)/(t_2 - t_1),$$

where v_2 and v_1 are the viscosity in poises at time t_2 and t_1 (in minutes), respectively. It has been found that the determined K value is often slightly different for different investigators. In the table are listed several values from the literature. It is well known that linseed oil varies somewhat in composition and iodine value; hence it is not surprising that some differences are found.

TABLE I

Bodying Constant of Drying Oils (6)

Oil	K × 10^3 at 300°C.	Reference
Linseed oil	3.2	(11)
Linseed oil	3.9	(14)
Linseed oil	4.4	(5)
Linseed oil	5.7	(7)
Linseed oil average	4.2	......
Dehydrated castor oil	8.8	(16)
	K × 10^3 at 250°C.	
Linseed oil	0.7	......
Tung oil	43.0	......
Tung oil	55.0	......

The change of this constant with temperature may be expected to be measured by the relationship (6)

$$d \operatorname{Log} K/dt = Q/RT^2,$$

which on integration gives

$$\operatorname{Log} K = Q/RT + B,$$

where R is the gas constant, T the absolute temperature, and B is a constant, and Q the heat of activation of the bodying reaction. From this it follows that the bodying constant should vary inversely as the absolute temperature. It will be seen in Figure 9 that, when the rate constants are plotted against the inverse of the absolute temperature, linear plots are obtained.

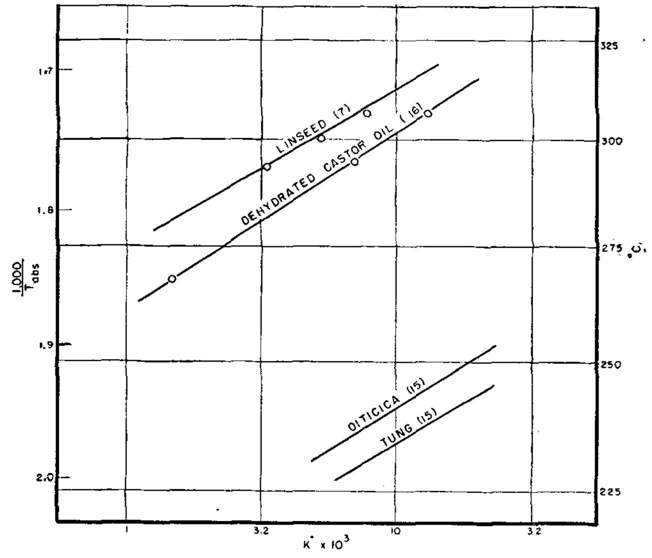

FIG. 9. Bodying rate and temperature.

Catalysts. It has been found that catalysts may greatly accelerate the bodying of oils. Since there are several steps in the reaction, a catalyst may be effective in promoting one step and, if this is a slow step in the reaction, the whole bodying reaction is accelerated. Isomerism to a conjugated form is the first step in the heat bodying of unconjugated oils and is a slow reaction. Thus anthraquinone and other polynuclear aromatic quinones have been shown to promote formation of conjugated structures (10) and are catalysts for the bodying of nonconjugated oils. Sulfur dioxide has been found to accelerate the bodying of linseed oil but has little effect on tung oil (6).

On the other hand, strong acid catalysts are shown to be powerful catalysts for the polymerization of olefins. Aluminum chloride, sulfuric acid, and other acid catalysts greatly accelerate the polymerization of drying oils. The reaction is often difficult to control and often leads to discoloration. Also removal of acidic catalyst residues is often difficult; hence such materials have not been extensively used with the drying oils. Boron fluoride also is effective in promoting polymerization. Oxygen is also effective in accelerating polymerization. However this effect is not catalytic and leads to darkening of the oil.

Effect of Degree of Unsaturation. It is readily apparent that the more unsaturated glycerides body much more readily than the more saturated glycerides. It was however only recently that it was recognized that oleic acid esters will react with other acid groups (2, 12). Oleic esters will not polymerize by themselves but, in the presence of more unsaturated acids, apparently enter into the polymerization to a moderate degree. By carefully measuring the rate of bodying of unconjugated oils and mixtures, an empirical relationship between the fatty acid composition and rate of bodying was achieved (2), which was determined by multiplying the content of oleate, linoleate, and linolenate esters by 0.6, 1.6, and 2.0, respectively. This gave a smooth curve when the sum of these products was plotted against the bodying rate constant of the samples.

It was felt that a straight-line relationship might be obtained if the second-order nature of the bodying reaction were taken into consideration. It was found that a linear relationship could be established by multiplying the linolenic content by 4.5 and the linoleic content by 2, and squaring the sum; the resulting value divided by 1,000 was equal to the determined rate constant of the oil (Figure 10).

$$K = (4.5\,LE + 2\,LO)^2/1{,}000$$

It is felt that this does not vitiate the activity of oleate esters; their activity however is dependent on the presence of more unsaturated esters whose presence will control the rate of bodying.

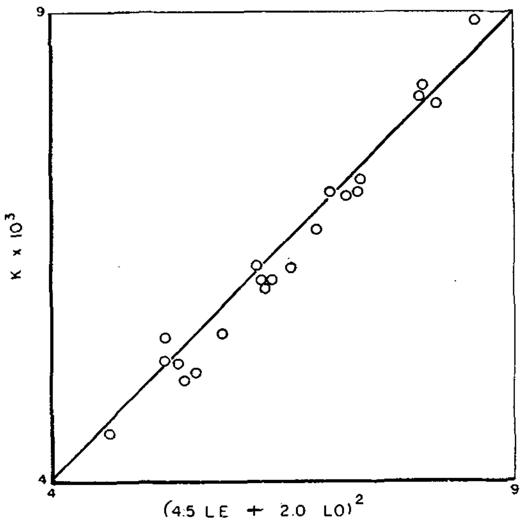

FIG. 10. Oil composition and bodying rate.

It is apparent that a reasonable estimate of the rate of bodying of many oils can now be arrived at from a consideration of the composition. Analysis of the behavior of mixtures of conjugated and non-conjugated oils should be carried out and correlated with the composition of the oils and their mixtures.

Liberation of Fatty Acids. When oils are bodied at temperatures of 300°C. and above for any prolonged time, the acid value shows a pronounced increase. If, as is occasionally done in the laboratory, bodying is carried out under vacuum, the liberated acids are largely removed with the volatile products. Attempts at continuous bodying at quite high temperatures have not been too successful, partly because of the high acidity of the bodied oils formed. The fact that liberated acids do not re-esterify suggests the possible formation of diglycerol esters.

Utilization of Bodied Oils

Heat-bodied oils are often used in paints and varnishes and are added to varnishes to check the bodying reaction. Bodied oils have been found to have considerably better durability than unbodied oils on outdoor exposure. To effect drying of an oil a certain amount of oxygen must first combine. The groups introduced by addition of oxygen in the drying-oil structure are focal points for the degradation reaction. The use of heat-bodied oils reduces the amount of oxygen necessary to effect the drying of the film and thereby improves its stability.

It is interesting to note that the dimer acids, formed by the heat treatment of fat acids, can be combined with the drying oils as are other dibasic acids in the formation of alkyd resins. These products have many properties of alkyd resins and indeed they should, but they also have much in common with bodied oils.

Heat bodying of oils is often carried out in the presence of natural or synthetic resins. Often the temperature required to disperse the resin is in the range usually employed in heat bodying. Thus some of the harder, less soluble resins cannot be used with tung or oiticica oils by conventional methods since the oils would gel before the resin was dispersed.

Since it is often undesirable to have unbodied oil present in a varnish, bodied oils are added to the varnish to chill it when the desired viscosity has been obtained.

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Blowing Drying Oils

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BLOWING with air or oxygen is a process applicable to all types of oils and fats. Hilditch states (11), "In many cases, especially with palm oils and tallows, it is possible to affect considerable bleaching by agitation with a current of air at 90-120°C. in enamelled, tinned, aluminum, or plain iron vessels."

W. L. Taylor

Blown whale and fish oils are used in stuffing greases for leather. Blown rapeseed oil and blown cottonseed oil are used in lubricants. The demand for blown unsaturated oils of the type with which we are concerned is evidenced by the fact that the Drying Oils Index of 1949, published by the Scientific Section of the National Paint, Varnish, and Lacquer Association (24), lists some 128 brand names of blown linseed, soybean, and fish oils. In addition, blown oils in considerable amounts are sold under brand names which are not listed or are prepared by various industries for use in their own plants. Also, blowing is recognized both in this country and abroad as a standard procedure in the preparation of the "boiled" oil used by house painters. Linoleum, which is the subject of a separate paper, has provided an outlet for fatty oils, mostly air oxidized, in such quantities that the Bureau of the Census lists the linoleum industry as one of the principal consumers of technical oils.

Equipment

When commenting on the methods of conjugation, Cowan (6) states that blowing with air or oxygen is probably the oldest and is effective in promoting both conjugation and polymerization. Under the circumstances it is only natural that many devices are described in the literature for speeding up oxidation. Large oil surfaces may be exposed to a current of air. The air, or the oil, may be warmed. The oil may be agitated mechanically while air is blown through it, but if sufficient air pressure is maintained, no mechanical agitation is needed. On the other hand, the oil may be blown as a spray into a tank and recirculated until the desired degree of oxidation has been obtained. The design of the blowing equipment is