The Significance of Tests on Drying Oils

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CHEMICAL and physical tests are commonly applied to drying oils for three purposes: a) control of quality; b) control of processes; c) investigative work to determine composition. For control of quality, buyer and seller most often use the following tests:


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- Iodine Value
- Acid Value
- Saponification Value
- Specific Gravity
- Color
- Viscosity
- Drying Time
- Foots Test
- Heat Break
- Percentage of Volatile Matter

Less commonly applied are refractive index, unsaponifiable content, hydroxyl value, and the Liebermann-Storch test for determination of rosin.

For control of processes, a manufacturer most commonly uses acid value, viscosity, color, iodine value, percentage of non-volatile, and drying time. Less often used are refractive index, saponification value, hardness and flexibility.

For research or investigational work the above tests are used as well as methods for hexabromide values, thiocyanogen values, neutralization equivalent, spectrophotometric determination of dienes, trienes and tetraenes, and many other lesser known tests and analytical methods. For research purposes, special analytical procedures are aimed at determining or characterizing specific modifying chemicals.

It is the purpose of this paper to discuss the more common of these tests and their significance in application. Time will not permit a thorough discussion of all the tests and analytical methods. Necessarily some must be touched upon only lightly. In the beginning it is of prime importance to recognize that fatty oils are not pure compounds. They are esters of mixed fatty acids. Hence the final properties of such oils are controlled by the kinds and proportions of fatty acids present and a limit is set on the significance of any one test. In order to get a complete picture, a multiplicity of tests must be run.

Iodine Value

Fatty oils are commonly classed as drying, semi-drying, and non-drying in accordance with their iodine values, thus providing an excellent illustration of the limitations of a single analytical test. The accepted rating scale is approximately as follows:

Drying oils, I.V.—160 and up
Semi-drying oils, I.V.—120 to 160
Non-drying oils, I.V.—below 120

The iodine value is an empirical determination requiring close attention to manipulative detail. The Wij's procedure, which is almost universally used in this country, measures the absorption of iodine monochloride by the sample, and the results are expressed in percentage of iodine absorbed. The numerical values obtained are dependent upon the concentration of the reagent, the excess of reagent over double bonds present in the sample, the time of absorption, the temperature of the absorption, and the presence of light during the absorption.

A uniform reagent is specified in practically all iodine value methods, and the reagent excess is controlled by varying the sample size. For non-conjugated oils such as soybean or linseed oils, essentially similar results are obtained over the wide range of reagent excesses from 100% to 300% of the amount absorbed, and a reagent excess of 125% ± 25% assures uniformity of results. With a conjugated oil such as tung oil, on the other hand, there is an increase of 2.5 units in going from 100% to 150% of reagent excess, and more rigid specification of excess reagent at 125 ± 10% has been found necessary.

Similarly non-conjugated oils are relatively insensitive to reasonable temperature variation during the absorption step. In the range from 20°C. to 30°C. there is less than 0.5 unit change in the iodine value of linseed oil. Tung oil increases in I.V. by 2.5 units in this range. A permissible temperature variation of 25° ± 5°C. has been adopted by the A.O.C.S. for non-conjugated drying oils and 25° ± 1°C. for conjugated oils with a uniform absorption time of one hour in the dark.

That I.V. is an inaccurate measure of drying ability is demonstrated by the fact that because of the variation in composition, fish oil with an I.V. of 195 does not dry as well as linseed of I.V. 178. Likewise safflower oil of I.V. 150 dries almost as well as linseed and much better than soya having an iodine value in the region of 135. In the latter case from the arithmetical difference in I.V. rating one would expect safflower to dry somewhat better than soya but not nearly so well as linseed. Such is not the case.

To carry the illustration further, tung oil, the fastest drying of all the vegetable oils has an I.V. of only 165. The very fast drying properties at a relatively low I.V. are caused by the presence in tung oil of a large proportion of a fatty acid, eleostearic, having a conjugated double bond system. This acid does not give a true I.V. under the conditions of the commonly used Wij's method even though it has the greatest affinity for oxygen of all the drying oils.

Such is also the case with oiticica oil and such synthetic or modified oils as dehydrated castor and maleic treated soya oils, all of which dry faster than their I.V.'s would indicate when rated according to the arbitrary scale ordinarily used.

Thus it is apparent that I.V. is useful as a means of identification of various oils when coupled with other tests and of variations of a single oil, but of little use as an absolute measurement of drying ability.

Quantitative hydrogenation has had limited application as a research tool for measurement of total unsaturation, but specialization of the apparatus and technique involved has prevented widespread use as a general analytical method.

Acid Value

Perhaps the most frequently used chemical test of drying oils is that of acid value. By definition, acid value is the number of milligrams of potassium hydroxide required to neutralize the acids in one gram of sample. Hence it is an expression of the free fatty acid content of a fatty oil.

The acid value is of importance to the processor of oils as an indication of quality of raw oil, as a control measure in the production of refined oils, and as a control test and measure of quality in the production of blown, bodied, and chemically modified oils. The test is indispensable in control of esterification reactions.

To the user of drying oils, acid value is one indication of quality of raw oils and is important as a specification test because of the influence of free fatty acids on paint properties. Acidity plays an important role in both the physical effect of wetting of pigments and the chemical effect of reactivity of certain pigments; consequently the free fatty acid content of an oil may cause a wide variation in viscosity, thixotropy, and application properties of paints. Excessive reactivity may even cause solidification of paint in the can and consequent loss of utility.

Acid value is a definite measure of quality of the fatty acids of commerce as used for the manufacture of soaps, alkyd resins, etc. In conjunction with saponification value the acid value is used to measure the purity and consequent value of such fatty acids.

In research work the acid value is not always a sufficiently accurate characteristic, and the analogous neutralization equivalent is used. This is run in the same manner as acid value but is calculated as the number of grams of sample which will combine with 56.11 grams of KOH. Thus the molecular weight of the fatty acid is taken into consideration.

Saponification Value

Acid value provides a measure of the free fatty acid present in a sample of oil, and saponification value is commonly thought to provide a measure of the combined acids in an ester. Though this is true in non-drying oils, it is not strictly so in drying oils because of the presence of alkali reactive groups other than carboxyl. Hence the Methods of Analysis of Drying Oils of the American Oil Chemists' Society specify the saponification value as follows: "the saponification value is a measure of the alkali reactive groups in fats and oils and is defined as the number of milligrams of potassium hydroxide required . . ." and gives as the scope of the method: "applicable to all natural and synthetic drying oils and their fatty acids."

With these limitations saponification values are useful for providing information as to quantity and type of glycerides and acids in a given sample. The saponification value provides a direct relative measure of the mean molecular weight of the acids in the sample. Short chain acids such as lauric have high saponification values while longer chain acids give correspondingly lower values.

Blown oils have higher saponification values than heat polymerized oils of the same viscosity. Maleic anhydride has an extremely high saponification value as do several other commonly used dicarboxylic acids. Rosin acids have a higher saponification value than do the common drying oil acids. Thus we see that this test, in conjunction with others, may be used as a quality control and a means of identification.

The procedure for determining saponification value involves refluxing 4 to 5 grams of sample with 50 ml. of standard alcoholic KOH for one-half hour. The unreacted base is then titrated with acid and the value calculated as the number of milligrams of KOH required to react with one gram of sample.

For research purposes the saponification equivalent is sometimes used. This value is run in the same manner as saponification value but is calculated as the number of milligrams of sample which will react with 56.11 grams of KOH. Expressed in this way, the numerical results are a measure of the average equivalent weight of the ester groups.

Unsaponifiable Matter

Since drying oils are esters of fatty acids and glycerol, any material which is not saponifiable (i.e., fatty acids) or water soluble (i.e., glycerol) must be a contaminant or a modifying agent. Thus the determination of unsaponifiable matter is important as a test for purity and as a means of identification of modified drying oils.

According to the methods of analysis of the A.O.C.S., unsaponifiable matter is defined as "substances frequently found dissolved in fats and oils which cannot be saponified by the caustic alkalies but which are soluble in ordinary fat solvents. Included are higher aliphatic alcohols, sterols, pigments, and hydrocarbons." This determination is a continuation of the saponification value procedure. The sample is first saponified with excess KOH and then washed several times with petroleum ether. The ether layers are drawn off and evaporated to dryness. The dried residue is weighed and the result expressed as percentage of original sample weight. Since free fatty acids are soluble in ether, a correction for their presence must be made.

Raw vegetable and fish oils contain phosphatides, sterols, proteinaceous material, etc. Unduly great amounts of such materials are detected by the unsaponifiable procedure. Resins, mineral oils, waxes, and other modifying agents are also isolated by this method. Thus the purposes of quality control and identification are served.

Hydroxyl and Acetyl Values

The hydroxyl and acetyl values are two closely related analytical determinations which measure the free hydroxyl content of oils and fats. The older acetyl value which expresses the results as the number of milligrams of KOH equivalent to the acetyl groups in one gram of acetylated sample has been almost wholly superseded by the hydroxyl value which bases the hydroxyl content on the original sample basis. The two values are readily interconvertible by simple calculations.

The older procedure involved acetylation of the sample, using an excess of acetic anhydride and measurement of the differences in saponification values of the isolated acetylated product and the original sample. Now more commonly the hydroxyl value is determined by measuring directly the amount of excess acetic anhydride remaining after reaction of the sample with standard acetic anhydride in pyridine.

Castor oil having a large proportion of the hydroxy acid, ricinoleic, has a large hydroxyl value, but in other unmodified oils the method measures the usually small content of hydroxy acids together with diglycerides and monoglycerides formed by partial hydrolysis of triglycerides. More important perhaps is the use of the method to determine the extent of esterification and alcoholysis reactions and the potential reactivity of various polyhydric alcohols used for oil modification.

Diene Value

The diene value of drying oils measures the conjugation and is expressed on the basis of number of centigrams of iodine per gram of sample in the same way that I.V. is expressed. Oils containing conjugated linkages such as tung, oiticica, and dehydrated castor oil react with maleic anhydride in a Diels-Alder reaction, and excess of reagent is determined by washing with water and titrating.

The diene value procedure has assumed less significance recently since the ultra violet spectrophotometer provides a more basic method for determination of conjugation. In addition the spectrophotometric procedure readily differentiates between triene conjugation, such as we have in tung and oiticica oils, and diene conjugation, as in dehydrated castor.

Foots Test

The preceding methods have comprised the most important chemical tests applied to drying oils. As a transition from these to the purely physical tests we must include a physical-chemical method which is the basis for much controversy, the foots test. The actual purpose of this test seems to be lost in antiquity, but it is probably meant to measure the non-oil materials present in raw linseed oil. Or perhaps its purpose is to measure the amount of "solids" which will sludge out of raw linseed oil on standing. At any rate, it is an empirical, inexact test which is written into many specifications and which is difficult of duplication between laboratories.

This test is run by introducing into a burette-like tube 25 ml. of oil and 25 ml. of acetone. To this is added 10 ml. of saturated acidic calcium chloride solution, and the mixture is shaken for exactly 1 minute. (Imagine efficient shaking in a burette!) The burette and contents are allowed to stand vertically for 24 hours, and the volume of the cloudy foots layer is read to the nearest 0.1 ml. This volume is multiplied by 4 to give the reportable result. Determinations are run on oil samples which have been heated and samples which have been chilled.

Because of the importance of pretreatment and of physical state of the foots in the oil, wide variations in results are commonly obtained. That there is a need for a test to measure what the foots test is supposed to demonstrate cannot be denied, but the present method definitely is not satisfactory. Both A.S.T.M. and A.O.C.S. committees are studying this matter at present.

Break Test

The idea behind this test is similar to that of the foots test, i.e., measurement of non-oil materials present in raw or crude oils. It is a much more accurate analytical procedure, and results are more easily duplicable than in the foots test. The break test is run by heating to 550°F. a sample of oil to which has been added a few drops of HCl. Non-oil material separates and after cooling is filtered off, washed free of oil with carbon tetrachloride, dried, and weighed. The result is expressed as percentage of total sample. Although this test is not used as widely in specifications as is the foots test, it has much to recommend it.

Viscosity

Of the physical tests viscosity is probably used more often than any other. It is important to the processor of oils as well as the user. Many paint properties are dependent on close control of viscosity. The body of paint, the flow of printing inks, the flow of enamels, and the fullness of varnish films are all dependent to some extent on viscosity. Hence the user must be certain that his oil and varnish vehicles have the proper viscosity and calls upon the processor to exercise great care in the control of viscosity of the materials he manufactures.

Viscosity is the primary control in the manufacture of varnishes, bodied oils, blown oils, and many modified oils. As a rule at a given reaction temperature, viscosity plotted against time will give a straight line curve on semi-log paper. This is of immeasurable assistance in predicting the end point in the manufacture of special oil products, allowing close control without elaborate equipment.

Many devices are used for determination of viscosity: efflux types such as the Ford cup, the A.S.T.M. cup, and the Parlin cup; capillary tube devices such as the Ostwald viscosimeter or the A.D.M. horizontal capillary type of viscosimeter, torque measurement machines such as the McMichael and the Brookfield viscosimeters; and falling ball and rising bubble methods. The last, as exemplified by the Gardner-Holdt tubes, is probably the most widely used. It has a decided advantage in simplicity and speed. The bubble viscosities are expressed in stokes, whereas other viscosimeters measure the basic cgs. unit, poises.

Color

When a householder buys a can of white paint or enamel, he expects it to look white in the package as well as when he brushes it on a surface. It follows that the manufacturer will use a light colored vehicle to make his white paint. The measurement of color of oils is therefore of major importance. In spite of this the methods now in use are comparatively crude. The most commonly used is the Gardner color system which comprises the comparison of a sample in a designated glass tube with standards in similar tubes. Colors are read on a numerical scale of 1-18, the smallest number denoting the lightest color. The Hellige comparator is essentially the same system but makes use of colored glass discs rather than liquid standards.

Both of these methods have the virtues of speed and simplicity if not of accuracy of characterization. Progress is presently being made in the devising of new systems of measurement of color of oils. Recently the American Oil Chemists' Society has approved a tentative new method for spectrophotometric determination of color at four wave lengths and by a formula reducing the color to a simple number. It is to be hoped that such a system will gain wide acceptance in the future.

Specific Gravity

The paint manufacturer buys drying oils by the pound but sells it, in the form of coating, by the gallon. Hence the specific gravity (or its analog, weight per gallon) is of prime importance to him in figuring costs. Refined soybean oil has a specific gravity of 0.924, raw linseed oil 0.931, and a blown or bodied oil may exceed 1.01. This spread in specific gravity when applied to a paint formula can have important technological effects as well as a bearing on costs.

Specific gravity is commonly determined by orthodox methods in a pycnometer or weight per gallon cap. Proper temperature control and accurate weights are the prerequisites for this test. Specific gravity is also used as a control method in the manufacture of blown oils since the increase in density is proportional to the amount of oxygen absorbed.

Percentage of Non-Volatile

The percentage of non-volatile, or percentage of solids, of a drying oil or coating vehicle which has been admixed with a volatile solvent is important for both specification and formulation use. The buyer wishes to pay on the basis of the film forming non-volatile portion and demands an accurate accounting of both solids and solvent. For his protection he runs a non-volatile determination, generally by the oven method. This consists of accurately weighing a sample which is heated in an oven at 105°C. for a specified length of time, or to constant weight and reweighing. Final weight, divided by sample weight, gives percentage of non-volatile.

As is the case in many seemingly simple tests, percentage of non-volatile is beset by difficulties. Oxygen absorption increases the weight of the residue and gives a false result. Or the sample may "skin over" because of surface drying of the sample and prevent evaporation of solvent from the subsurface. Or further, false low results may be obtained because of release of volatile products formed by the baking of the vehicle. No method yet devised is absolutely accurate; consequently the industry generally accepts non-volatile determinations on the basis of plus or minus 1% accuracy.

Moisture determinations as such are relatively unimportant in drying oil technology. The presence of more than traces of moisture is readily apparent by visual clouding, and larger quantities constituting gross contamination are evident by phase separation.

Gel Time and Heat Bodying Test

In the manufacture of varnishes, drying oils are heated with resins until the mixture becomes extremely viscous. Often, in order to get heavy varnishes, the polymerization is taken to incipient gelation. It is important therefore that the varnish maker know how fast an oil will body or, in the case of the conjugated oils, how quickly they will gel.

This information is provided by heat bodying and gel time tests. The former involves heating a 700-g. sample of oil in an insulated stainless steel beaker at 585°F. to the gel point. Viscosity and color determinations are made at half-hour intervals. The viscosities are plotted against time on semi-log paper and the corresponding colors noted. This gives a graphic picture of the rate of polymerization and of the color stability of the oil.

In the gel time determination a 5-ml. sample is heated at 540°F. in a test tube containing a stirring rod. The gel end point is taken as the heating time in minutes such that lifting of the stirring rod will raise both the oil and test tube.

Flash Point

The flash point determination is usually applied to oils which have been thinned with a volatile, inflammable solvent. In this test the oil is slowly heated and a small open flame applied to its surface at intervals as the temperature rises. The temperature at which the vapors above the surface flash by ignition is called the flash point. This test is important for reasons of safety in handling and shipping.

Acetone Number

A comparatively new test that is of importance in quality control of bodied oils and of some use in research is the determination of acetone number. To obtain this value use is made of the fact that acetone is freely soluble in unpolymerized oil but not in polymerized oil. This method is simply a titration of oil with acetone to a permanent cloudy end point, and the result is expressed as the percentage by weight of acetone added to the sample.

This test is of value in determining the uniformity of polymer distribution in bodied oils. Expert use of acetone number will indicate whether oils have been bodied at high or low temperatures and whether viscosity control has been attained by blending high and low viscosity components.

Spectrophotometric Analysis

Examination of drying oils by ultraviolet spectrophotometry serves two distinct purposes. When used on samples on an as-is basis, the procedure permits determination of diene, triene, and tetraene conjugation. Isolated double bonds do not have a characteristic absorption in the near ultraviolet region. On the other hand, conjugated dienes absorb light characteristically in the ultraviolet at 233 $m\mu$, and conjugated trienes and tetraenes similarly absorb light at longer wave lengths of 268 $m\mu$ and 316 $m\mu$. The intensity of the absorption at each wave-length is proportional to the amount of conjugation present, permitting quantitative estimation of the different conjugated components.

In the presence of alkali at high temperatures, non-conjugated unsaturated fatty acids are partially converted to the corresponding conjugated isomers. By using carefully standardized conditions of alkaline treatment involving close control of time and temperature, the extent of alkaline conversion can be reproduced quite closely. The alkaline conjugation procedure followed by spectrophotometric analysis permits quantitative determination of di, tri, and tetra unsaturated components in drying oils and, when coupled with a separate determination for saturated acids, a complete fatty acid analysis of a drying oil.

There is a third and up to now little used possibility of spectrophotometric analysis for determination of trace constituents. A variety of components normally present in oils such as chlorophyll, carotenoids, tocopherol, etc., can be precisely characterized and measured.

Contamination of an oil such as linseed by a material such as fish oil can be readily observed by the abnormally large proportion of tetraene conjugation after alkali isomerization of the sample containing fish oil. A host of unexplored possibilities lies ahead in the analysis of oils modified with resins and other agents.

Drying Time

The primary feature of a drying oil is its ability to convert from a liquid vehicle to a solid film upon exposure to air. It follows therefore that the measurement of this property is one of the most significant tests to be applied to a drying oil. It would seem that this should be a simple process. Yet the fact remains that no wholly satisfactory mechanical device has yet been invented for determination of drying time, and seldom do results of several operators agree when the ancient "finger-touch" method is applied. This is due to several factors:

a) drying time is profoundly affected by temperature, humidity, amount and kind of light, and movement of air past the film surface.

b) amounts and kinds of metallic driers used can cause variations in results. The manner of incorporation of these driers and the length of time of contact of drier and oil also have effects.

c) drying is greatly affected by thickness of film.

d) in drying, an oil passes through several physical stages which are difficult to define.

The a, b, and c above are amenable to physical control. Drying time tests are generally run in cabinets or rooms having controlled temperature and humidity. Definite proportions and procedures can be specified for the addition of driers. Films of definite, uniform thickness can be laid down by mechanical means. But the definition and conception of what is "set to touch," "dust free," and "dry hard" still remain difficult.

In the "finger touch" method the operator determines several end points by touching a drying film with the tip of the finger. (An obvious prerequisite is a clean, dry finger, but this is not always attained.) When the oil has reached a tacky condition and none is transferred to the finger under light pressure, it is said to be "set to touch." When the finger may be drawn lightly over the surface without deforming the film or feeling a stickiness, the oil is said to have dried to the "dust free" stage. When pressure between the finger and thumb causes no deformation or marking, the coating is said to be "dried hard." Note these three stages of drying. There are several more stages used by some technicians, and there are other definitions. However the above are fairly well accepted. When you have these firmly in mind and have made the test 20 or 30 times, you are just as much an expert on drying time as anyone else.

Seriously speaking, a tremendous amount of work has gone toward devising a suitable drying time test. This is witnessed by the fact that today numerous devices are being used and studied for this purpose. A partial list would include the Sanderson meter, the Paraffine Company machine, the Parks Dry-O-Graph, the Gardner Drying Time Recorder, the Rolling Ball tester, the Swinging Beam tester, the Sward Rocker, the Gardner Magnetic Tack tester, the Zapon Tack tester, the Nuodex Touch Controller for tack free time, the Blom test, and the RCI Drying Recorder. Many of these devices have merit and give excellent comparative results but do not detect the stages defined above.

In summary, it may be repeated that because of compositional variations no single test may be used to characterize a drying oil. A multiplicity of analytical results is necessary to accomplish this. There are numerous accurate, reliable test methods, but several must be used with caution and with a knowledge of their limitations. All must be used with intelligence. There is a tendency in the industry to "run tests" without regard to their limitations or utility. This should be discouraged since specifications in general are too complex. That there is a need for standardization and clarification of many test methods is recognized by processors and users, and progress is now being made in this direction.

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