DETERMINATION OF THE IODINE ABSORPTION AND FOOTS FORMATION OF LINSEED OIL

BY GLENN H. PICKARD

The examination of commercial as well as edible oils is divided into two distinct considerations, purity and quality. Just as it is possible to have a perfectly pure edible oil that is unsatisfactory for use as a food because of off-flavor, for instance, so it is possible to have a pure oil, such as linseed or china wood, which is unsatisfactory for use because of certain properties which it possesses or lacks.

There has been considerable study of the quality of linseed oil, one of the most important industrial oils of our commerce. The American Society for Testing Materials, through Committee D-1 on protective coatings, and through a sub-committee of this committee on linseed oil, has conducted a study of both purity and quality over a period of several years. A resumé of the work of this committee is fraught with interest.

Iodine Number

The iodine number, which measures the percentage of iodine absorbed by an oil, is an important indicator of both purity and quality. It measures the number of double bonds or unsaturated linkages in the hydrocarbon chain of the oil molecule. Because the number of these linkages is characteristic of various oils, and because the drying power of an oil is dependent upon the number of these unsaturated linkages, the iodine number is a measure of both purity and quality. It is not, however, an absolute measure of either, for the number of unsaturated linkages varies with the same oil, dependent upon agricultural conditions obtaining during the development of the seed. Also, the total of double bonds measured by the iodine number does not necessarily fully measure quality. Two oils of the same iodine absorption may yield films varying in elasticity, hardness and toughness because of the distribution of these double bonds. The qualities mentioned measure, to some extent, the service-giving properties of protective coatings of which the oil is a constituent.

The greater the degree of unsaturation in any molecule the harder and tougher will be the product of oxidation of that molecule. There are in linseed oil in varying amounts the glycerides of linoleic, linolic, oleic, and saturated acids, together with some mixed glycerides. The extremes of unsaturation are in linoleic acid with three double bonds, and oleic with one. The former dries to a hard, tough film, while the latter, even when completely oxidized, is still a viscous liquid. Linolin dries to a rubber-like solid. The unoxidized portions of an oil are dispersed throughout the film after drying, and tend to make it soft and cheesy. That is, they reduce simultaneously the hardness and the elasticity of the film.

It is obvious that a film produced by the oxidation of a mixture of linolein and olein would not possess the service-giving qualities of one which contained more linolin, the middle glyceride, because in the latter case the oxidation products would all be solid, whereas in the former the film would be a mixture of hard and soft portions. In other words, it is better to have a minimum of the extremes with more of the middle portion than the reverse. It is also clear that the iodine number would not indicate the distribution of the unsaturated linkages, and therefore absolutely indicate the quality. However, while the iodine number does not give a positive proof of quality, yet it is obvious that the higher the iodine number, the better the oil when used in protective coatings where its ability to oxidize is essential.

The methods of measuring the capacity of an oil to absorb iodine or oxygen are of interest. The first one of prominence to be employed was the Hübl method. While still used by some it is not so widely employed as it once was. The objections to it are the time required for absorption, the incompleteness of the absorption, and the lack of permanence of the solution. It has been found to give inaccurate results, especially on high iodine number oils. It has not been used on linseed oil for a number of years, though it is still employed by a few for china wood oil. The other methods in general use are those of Wijs and Hanus. The Wijs method is based upon a solution of iodine chloride in glacial acetic acid, while the Hanus consists of iodine bromide in glacial acetic acid. Both of these methods are very widely used today.

Some years ago the Association of Official Agricultural Chemists studied the methods for the determination of the iodine number. . They concluded that much better results are obtained by the Wijs and Hanus solutions than by the Hübl, and that the Hanus method gives results much more closely agreeing with the existing data than the Wijs. They made the Hanus method official at that time. When the American Society for Testing Materials began its work upon the iodine number they accepted the results of the Association of Official Agricultural Chemists, and accordingly adopted the Hanus method without investigation. As a consequence all of the existing data of this Society on the iodine absorption of linseed oil was obtained by the use of the Hanus method. A few years ago a committee on the analysis of commercial fats and oils of the American Chemical Society, after a careful study, recommended the use of the Wijs method for the determination of the iodine number. Their report said that this method was adopted after a careful comparison with the Hanus and Hübl methods. The Hübl method was eliminated from consideration almost at the beginning of the committee's work for the reason that the time required for complete absorption of the iodine is unnecessarily long, and in fact, even after absorption has gone on over night, it is apparently not complete. In the case of the Hanus and Wijs methods, complete absorption takes place in from fifteen minutes to an hour, depending on conditions. Formerly, many chemists thought the Hanus solution rather easier to prepare than the Wijs solution, but the experience of the committee was that the Wijs solution was no more difficult to prepare than the Hanus. Furthermore, absorption of iodine from the Wijs solution appeared to take place with greater promptness and certainty than from the Hanus, and was complete in a shorter time. Results by the Wijs method were also in better agreement in the case of oils showing a high iodine absorption for the same length of time. However, the difference was not great.

Recently the American Society for Testing Materials' Committee made a comparison of the results obtained by the application of the Hanus and Wijs methods upon linseed oil. Some of the reasons for the investigation were that the Hanus solution cannot be used to determine the iodine absorption of china wood oil or shellac, both important commodities closely paralleling linseed oil in distribution. Therefore it was necessary to have two solutions in laboratories where these three materials were to be tested. Obviously it was desirable to use one solution if such a procedure was found practicable. This situation was one of the reasons which led the American Society for Testing Materials to begin an investigation comparing the Wijs and the Hanus methods. The details of the procedure for the Wijs method were those recommended by the committee of the American Chemical Society, which worked them out for high iodine oils and also especially for china wood oil. The results obtained by this committee show that there is little or nothing to choose between the two methods from the standpoint of accuracy. In general the concordance between the various operators was very good by either method.

In work done during 1921 the average difference in per cent of iodine absorbed as measured by the two methods was $4^1/_2$ per cent. The results of the Wijs method were the higher, as was expected. In 1924, the average difference was 4.6 per cent. It therefore appears feasible in the case of linseed oil to convert results obtained by the Hanus method to their equivalent in Wijs figures by the addition of $4^1/_2$ per cent. This makes it practicable to change specification figures as well as to compare existing data obtained by either of the methods. Because there is no difference in the accuracy of the two, and because the Wijs method is more generally applicable, and because there will be no difficulty encountered in the comparison of existing data with that to be acquired, it is the writer's opinion that the Wijs method is the better one to use because of its wider applicability in the analysis of the materials used alongside of linseed oil, especially in the case of china wood oil and shellac.

Summing up, the American Society for Testing Materials has found that the iodine number is a very valuable indicator of purity and of quality, and that it should be an item of any specification; that it can be satisfactorily measured by the use of either the Wijs or Hanus methods; that the results obtained by the Wijs method will be approximately $4^1/_2$ per cent higher than with the Hanus; that the only weakness of the determination is that limits of such a spread must be used, because of the variation in the iodine number of pure linseed oils, that there is made possible an apppreciable adulteration of a high iodine oil with a low one without falling below a practical minimum. The quality indications of the iodine number are also somewhat akin to those of purity in that it is possible to have oils of practically the same iodine absorption which will yield products varying in important qualities.

Determination of Foots

Another indication of the quality of linseed oil is the amount of suspended or precipitated matter which it contains. This sediment is termed foots. The formation of it is gradual, proceeding at rates varying with the nature and composition of the oil and with the conditions obtaining during the period of separation. The foots of raw linseed oil comprise three main elements which vary in amount. They are, first, the high melting point, saturated fats which are solids at normal temperature; second, the so-called mucilaginous materials dissolved by the oil from the remaining portions of the seed during the crushing process; and third, water.

Obviously the amount of high melting point fats will vary with the composition of the oil, which, in turn, depends upon natural conditions prevailing during the growth of the flax plant. Inasmuch as these bodies are liquid above a certain temperature and solid below it, the amount present will vary also with the temperature at which filtration takes place. If that is below the point of solidification, removal will be accomplished, but if above, they will remain in solution.

The solubility of the mucilaginous materials is affected to a lesser extent by temperature, though a portion of the amount originally present in the freshly crushed oil is undoubtedly removed by filtration at comparatively low temperatures. Time is an important factor in the removal of this material, since a gradual precipitation occurs.

Moisture is dissolved by the oil during the operations of crushing. Generally speaking, the more moisture there is in the ground seed as it goes to the hydraulic press the more water there will be dissolved in the oil. The amount will, of course, be dependent upon the ability of the oil to dissolve it. Within certain limits the higher the temperature of the oil, the more water there can be present without producing a cloudy liquid.

All three of these materials are present in the oil in the colloidal state, which state in this case is not a permanent one. The result is that, as the oil ages, varying portions of all three separate out, thus improving the quality of the supernatant liquid.

To measure the amount of foots or potential foots in linseed oil has been a problem upon which much thought and effort has been expended by the American Society for Testing Materials.

The first test devised was one which allowed a measured volume of oil to deposit foots in a graduated vessel over a definite period of time. This method was found impracticable because of the time required, the varying density of the deposit, and the incompleteness of the precipitation. Later, precipitation from a solution of oil in petroleum ether was tried. This failed for the reasons just given, and also because of the variations in the solvent power of the different petroleum products used. Acetone as a solvent was next tested. It also gave unsatisfactory results when used alone. Walker and Wertz modified this method by employing with the acetone a ten per cent hydrochloric acid solution saturated with calcium chloride. This method has given greater satisfaction than any other, but the committee has found it so inaccurate as to prevent the inclusion of it as an item of a standard specification. Recently the effect of the variations in temperature upon the oil previous to the determination of the foots content was thought to account for discordant results. The oil was warmed before making the determination in order to eliminate such an effect, but the concordance of results, while improved, was not great enough to permit the test to be described as accurate.

The use of the centrifuge under standardized conditions was also tried, but it made no improvement in the results. In its last report, the committee said, "The results obtained are very similar to those obtained in previous years. There is the same lack of concordance that has always existed when this test has been applied to the same oil by different operators. There is also the same lack of concordance that has always existed when the same oil has been tested by the same operator after it has been subjected to varying conditions which it might meet in commercial practice, such as temperature variations. A variation in the method by heating the oil previous to mixing with the reagents improves the concordance slightly, but not sufficiently. The variables involved in the method seem to be too great to allow of satisfactory results. The sub-committee, therefore, must reluctantly reaffirm the position taken in its last year's report, namely, that neither this test nor any modification of it proposed to date is sufficiently accurate for use in standard specifications." The committee realizes the necessity for an accurate test for the determination of foots and potential foots, and is at present studying means of determining the amount of the "break," that is, the material which separates out when the oil has been heated to temperatures usually between 400 and 500 degrees Fahrenheit. Thus far the conditions under which this separation must be made have not been so closely defined that satisfactorily concordant results were obtained.

A study of the percentage of the ash of the oil is under way. Apparently, because of the variation of the amount of the ash of the different foots-forming materials this determination will not give satisfactory indication of quality. Because of the high ash of the materials which form the break, their presence in excessive amount will be indicated. But moisture and high melting-point fats will not be included. The elimination of the moisture is, of course, unimportant, because that can be determined in another way.

The situation as it now stands is that there is no satisfactory determination, or set of determinations for the estimation of the quality of linseed oil. There is, however, sufficient data to warrant the continuation of investigations to the end that quality determination can be satisfactorily and accurately accomplished.

IS THE BLEACHING ACTION OF FULLER'S EARTH DUE TO OXIDATION?

By Clarence W. Benedict

Fuller's Earth is essentially a clay. It differs from ordinary clay in that it is derived from Hornblende and Augite rather than from Feldspars. It contains hydrous aluminum silicates and has a marked colloidal structure.

A large amount of research work has been done on Fuller's Earth to determine just why it bleaches. The accepted theory has always been that the bleaching is the result of adsorption of the coloring matter by the earth.

However, this theory while generally accepted is as yet only a theory. Just why Fuller's Earth bleaches is still unknown. Dr. Wesson has advanced the theory that this bleaching power of Fuller's Earth may be due to oxidizing action of the earth upon the oil. This theory seems plausible in as much as oils can be bleached by treating them with strong oxidizing agents. It was the purpose of this study to determine whether or not oxidation had anything to do with the bleaching.

Procedure. The first step in the investigation was to determine the oxidizing power of the earth. This was done by weighing out accurately five grams each of twelve different earths, into 250 cc. volumetric flasks, and covering them with 50 cc. of carbonated water to drive out the air present and permit of working in an atmosphere of carbon dioxide. Next 25 cc. of Mohrs salt solution were added and the flasks filled to the 250-cc. mark with boiled, distilled, oxygen-free water. They were then shaken by hand for five minutes, allowed to stand and settle, until 50 cc. of clear liquid could be drawn off and titrated with potassium permanganate. Checks were made on each titration. Two blanks were run at the same