Furfuryl esters were found to polymerize to products of greatly decreased iodine number and increased acidity, showing that polymerization involved both deacylation and reaction at the double bonds of the furan ring.

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# **Report of the Bleaching Methods Committee** $1942 \cdot 1943$

This Committee was formed last year with the express purpose of studying the A.O.C.S. Bleach Test as applied to refined soybean oil, and the outcome of last year's work was the adoption as tentative of a slight modification in the method which had generally been used on cottonseed oil, as a result of which the method now shows two procedures for the bleach test, one for cottonseed and other oils and one for soybean oil.

This year there were two points presented for consideration by this Commtitee: (1) the desirability of wording the bleach test procedure to insure that the oil filtered for the color reading be absolutely clear and free from turbidity and (2) the question of yellow-to-red ratio.

1. Clarity. At least two Society members called attention to the fact that the oil might not be entirely clear when making the color reading, thus resulting in an inaccurate reading—higher than it should be. This apparently has obtained in spite of the wording of the method: "after sufficient oil has passed the filter to insure clearness . . ." It was the unanimous opinion of those of the Committee reporting on this that the insertion of the words "close textured" before the words *filter paper* would be a desirable change in the wording of the method which would lessen the likelihood of colors being read on slightly turbid testbleached oil. Hence the direction which now reads, ". . . and filter through filter paper," would then read: ". . . filter through an unused close textured filter paper." The Committee did not consider this point to be of sufficient importance to warrant a laboratory study of various filter papers leading to the designation of specific types or brands.

It should be pointed out to those who have been accustomed to using a fast-filtering paper that while the use of a more retentive paper in this application might appear at first sight to slow the outturn of results, it must be recalled that the large-pore, fastfiltering paper requires that a fairly large amount of oil be passed before it begins to come with sufficient clarity to yield an accurate color reading, so that it is doubtful if any appreciable time is lost. Moreover, the fuller's earth-oil mixture is poured into the filter paper at a temperature of 105°C. or higher, at which the filter rate is fairly rapid even through a highly retentive paper.

2. Yellow-to-red Ratio. The Committee was practically unanimous in the opinion that bleach colors on soybean oil cannot be satisfactorily read using the ten-to-one yellow-red ratio now designated in our methods for colors under 3.5 red or using the fixed 70 yellow value for colors higher than 3.5 red, especially in times when the oil contains appreciable chlorophyll, or when it is off-hue due to other causes.

[This question has assumed an enhanced importance commercially within recent weeks as the result of the recommendations of a Task Committee convened by the Office of Price Administration, providing a scale of discounts for off-bleach color on crude soybean oil. The yellow-to-red ratio was considered by the oil chemists present (representing the soybean oil industry), and the scale of bleach colors was given in terms of the red reading, with the yellow color being read as is, in other words, with the yellow which affords the best match. This action was considered by the Finished Materials Standards Committee and the Rules Committee of the National Soybean Processors' Association and approved by both groups.]

A careful reading of our method Section (b) Determination—under the section Refined Oils—Color (pg. 16f) reveals that the method as written now provides for the contingencies of oils not conforming to type and also where "Rules specify the yellow and/or red to be used in determining given grades." Thus "The ratio of yellow to red in determining color shall be as follows, except where rules specify the yellow and/or red to be used in determining given grades:

> Soybean Oil-10 yellow to 1 red, up to 3.5 red 70 yellow for 3.5 red or higher

"If the above ratios fail to give a satisfactory match, this fact should be noted and a second reading made, using the amount of yellow required for a good match. Report both readings.'

Nevertheless, the Committee recommends the addition of the following paragraph to follow the last paragraph in the directions just quoted:

"Note-Soybean Oils are subject at times to abnormalities in the composition of their pigment contents resulting in the occurrence of hues which cannot be matched even approximately using the fixed yellow or yellow-to-red ratio designated above. In the case of such oils, report only the reading with the yellow required to give the best match."

This recommendation is made with the thought that the reporting of two different color readings under such circumstances can serve no useful purpose and is likely to lead to confusion.

Consequent upon this action, the Committee further recommends that the first paragraph quoted above be changed to read as follows: "The ratio of yellow-tored in determining color shall be as follows, except where Rules specify 'yellow affording the best match,'

or where they specify the yellow and/or red to be used in determining given grades."

The question may reasonably be raised as to the wisdom of leaving a fixed yellow, and yellow-red ratio in our methods for an oil on which experience now provides so little support for the justification for the values designated. While the Committee does not favor these values, it believes them to have been put into the method as a result of a considerable experience and prefers at this time to make only the changes in wording recommended above, with the thought that in the coming year a considerable experience in reading bleached refined colors on soybean oil will be accumulated by which we will be in a better position after another year to judge further the wisdom of abolishing altogether any fixed yellow or yellow ratio.

Finally, the Committee would like to recommend to the Uniform Methods and Planning Committee two minor additions of an editorial nature to the method under "Color," (1) that the section heading, page 16f, now reading, REFINED OILS—COLOR be changed to read, REFINED AND BLEACHED OILS—COLOR; (2) in the second paragraph under the sub-heading, (b) DE-TERMINATION—let this paragraph have a sub-heading in appropriate type as follows: *Refined Oils*. Let the paragraph following this then be given the sub-heading, *Refined and Bleached Oils*. The Chairman came to the conclusion that these heading changes and additions would help clarify the meaning of the various paragraphs in the method on Color, as a result of puzzling back and forth through the method seeking out the exact meaning and intent in respect to the immediate question concerned in this report.

#### EGBERT FREYER, Chairman

G. Worthen Agee	RALPH MARMOR
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## **Fish Oil in the Protective Coating Field**

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SEARCH of the records of history for the birth or inception of fish oil reveals that it really never had one, and it may be assumed that, like Topsy, it "just grew." At least, there is no record of its discovery and no eminent sponsor to proclaim its virtue. Early records indicate that the fish caught along the coasts of France and Spain, and later along our Atlantic Coast, were used as food. The by-products, heads, scrap, and excess fish were converted into fertilizer. Lewkowitsch summarizes the background of fish oil in a single statement in which he writes, "and it is owing to the demand for fertilizer that the fish oil industry has assumed such large dimensions." Actually, the industry is relatively new, and again Lewkowitsch may be quoted as saying, in 1914, "The employment of sardine oil in the varnish industry can only be looked upon as an experiment which, doubtless, has led to failure."

During the past 30 to 40 years, the industry has grown tremendously and, in 1925, the following opinion is reported in Toch's Chemistry and Technology of Paints, "Results obtained from proper grades of fish oil warrant the use of fish oil in the hands of an intelligent manufacturer." While this statement, made 20 years ago, could not be referred to as enthusiastic, it is definitely an indication of progress. Practically all earlier references on fish oil were in error because the fish caught consisted of a mixed variety of low oil content. They were also improperly processed and partially putrefied in transportation. Therefore, we cannot attach too much significance to the reports of the earliest investigators, nor should we continue to retard the data they compiled as conforming to present day practice. This global war has increased the incentive in re-

This global war has increased the incentive in research to almost a fever pitch. Most of us, layman and chemist alike, entertained ideas on replacements for critical materials far from our own field of endeavor. Perhaps a few of us were specific or practical in our thinking. Washington authorities and civilians, as well, overtaxed themselves in advancing the determined stand that we were not to be defeated by shortages.

The outcome of this mad scramble to avoid the use of critical materials will be evident in the years that follow the war. However, the most cautious result that we may forecast is that it helped immeasurably in the obliteration of credulous thinking, fixed ideas, and unconfirmed opinions. In short, it brought us up-to-date. No one needs to be told that this war created a whole new set of values; they are self-evident and affect our daily lives. Perhaps, one of the most impressive changes that has been fundamental and necessary is the conversion from imported drying oils such as tung oil, oiticica, and perilla to oils of a domestic source.

Sponsored by consumer-demand and the progressive incentive of oil processors, fractionated fish oil products were developed that are sufficiently capable of replacing wood oil. Solvent segregated fish oil products, introduced in 1940, have been used to replace wood oil in finishes for landing boats, plywood gliders, metal food closures, marine and harbor installations, aircraft, and numerous other items.

Let us reflect upon this transition. In 1914, Lewkowitsch reported fish oil to be a failure in varnishes; in 1940, we find fractionated fish oils accepted as a wood oil replacement. Prior to 1940, fish oil products consisted of blown oils, kettle-bodied oils, and a few products treated with resin, other oils, lime, etc. All of these oils were used extensively in coatings that were designed to serve a specific purpose.

Blown oils were, and are at present, being used to contribute to the flow and leveling characteristics of

This paper was given in a symposium on drying oils at the New Orleans meeting on October 7, 1943.