Organic Peroxides as Bleaching Agents

Their Application in the Oil and Fat Industries

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BLEACHING is the art of eliminating coloring matters from products which generally have a vegetable or animal origin.

The methods used in bleaching are mostly oxidations or reductions by which the coloring matters are changed into colorless compounds which are either harmless or which can be eliminated easily. Besides these methods we have bleaching methods by adsorptive means.

It may be well to mention here the words of Lewkowitsch who says: "Too much stress cannot be laid on the necessity of regarding the bleaching of each individual oil or fat as a problem *sui generis*, and of recognizing that the processes adopted on a manufacturing scale must vary greatly with the nature of each individual oil or fat."

Coloring Matters in Oils

In solving the problem of bleaching a certain oil we first must try to determine the exact nature of the coloring matters. Unfortunately the chemistry of these substances is still a field wide open for speculation. In animal and vegetable tissues we find in the cells, together with the oil, coloring pigments which are named chromolipoids. This name is to be preferred over the old name of lipochromes (See Palmer, Carotinoids and Related Pigments. p. 18).

The red or yellow color of a refined oil or fat is for the greater part due to these chromolipoids. Very few of these chromolipoids are known in the chemically pure state. Tswett distinguishes a class of chromolipoids which he calls carotinoids and in which he brings all the various chromolipoids which are chemically and generically related to carotin. He designates as carotins all those chromolipoids whose constitution and properties show them to be hydrocarbons and as xanthophylls all those whose constitution and properties show them to be oxy-hydrocarbons and which are chemically, as well as generically, related to carotin. Palmer also adopts this terminology in his book: "Carotinoids and Related Pigments." (A. C. S. Monograph Series)

The two carotinoids which are best known as defined chemical individuals are carotin and xanthophyll. Carotin has the formula $C_{40}H_{56}$; Xanthophyll has the formula $C_{40}H_{56}O_2$.

Both of these substances are highly unsaturated and carotin is reported to be able to absorb twelve atoms of oxygen in its molecule. This oxidation is at the same time a bleaching. The characteristic red or yellow color disappears entirely.

Carotin, especially, is one of the principal coloring matters in the ordinary refined oils and fats. Therefore, we will study this substance a little closer.

Solutions of carotin are unaffected by boiling with alkalies, and therefore the refining of an oil does not destroy the carotin. Carotin cannot be absorbed easily by finely divided substances. Palmer describes his experiments with various decolorizing carbons.

In strictly adsorption experiments in which there was no indication that decolorization was due in part to oxidation of the carotin, he found that at least 12.5 grams of the most effective carbon so far obtainable was required to completely absorb the carotin out of 100 grams of fat.

In view of the above stated properties of carotin, which to a certain extent are also the properties of many other chromolipoids, the best way to destroy color due to one of these substances is through oxidation. The oxidation products of these substances are colorless; in other words through oxidation the intense red or yellow color can be bleached entirely.

Bleaching by Oxidation

It is not my intention to give a complete survey of all the different oxidation bleaching methods because these are described more competently and in detail in the various handbooks.

I will here describe a method which has not received much attention because the chemicals used are relatively rare. This process uses the organic peroxides as oxidation agents.

Organic peroxides may be considered as derivatives of hydrogen peroxide (H-O-O-H) in which one or both hydrogen atoms are replaced by a single or bivalent group, or even a more complex structure. The best known organic peroxide is benzoyl peroxide with the correct scientific name of di-benzoyl peroxide.

Di-benzoyl-peroxide is a crystalline substance with a melting point of 103.5°C. It is soluble in oil. Although many other organic peroxides are equally interesting from a chemical standpoint and research work on them is at present in progress, we will restrict ourselves here to benzoyl peroxide. Formerly this compound belonged to the rare chemicals, but at present it is manufactured on a large scale. Its use as a flour bleach is patented, and a product containing benzoyl peroxide is obtainable in the market, as is pure benzoyl peroxide also.

In working out a satisfactory method for the bleaching of an oil with benzoyl peroxide, three factors have to be determined.

1. Percentage to be used.
2. Temperature at which best results are obtained.
3. Time in which best results are obtained.

1. The percentage of benzoyl peroxide to be used varies from 0.05% to 0.2%. By running a series of bleaching tests on small samples of oil, varying this percentage and keeping temperature and time the same in all the tests, the most economical percentage can be determined.

2. A temperature of 80°-90°C. gives as a rule the best results. At higher temperatures a slow decomposition of the benzoyl peroxide starts and there is a loss of bleaching strength. Sometimes lower temperatures give better results.

3. The time of the treatment varies greatly with the nature of the oil. Sometimes a twenty minute heat treatment is sufficient. Sometimes even after a few days an after-bleaching effect is seen.

The method of bleaching is very simple, and can be outlined as follows. After determining the above three factors in the laboratory, a factory batch of oil is heated to the right temperature. In the meantime, the necessary amount of benzoyl peroxide is made into a paste with a small portion of the oil, until all the lumps are pulverized. Then the mixture is added to the heated oil, care being taken that all benzoyl peroxide is dissolved before more paste is added. A thorough stirring is necessary. Benzoyl peroxide is very soluble in oil, but it must be remembered that only the benzoyl peroxide in actual solution can produce the desired bleaching effect. Therefore, any particles which might not dissolve will decrease the efficiency of the process. After stirring for the necessary period, the oil can be left to itself. As no deposits are formed, no filtering is therefore necessary. This makes the benzoyl peroxide treatment stand out from all other bleaching processes, all of which make it necessary to eliminate precipitates or emulsions which are formed, resulting in inevitable loss of fat or oil. After the benzoyl peroxide has produced its bleaching effect and lost its available oxygen, there remains a small amount of benzoic acid. Because of its great volatility, the greater part of this benzoic acid disappears in the bleaching process. The remaining amount is so small that it can hardly be detected, and especially after steaming or deodorizing the oil, there is no trace of benzoic acid left.

At present research work is being done on a great many oils and fats, in connection with the organic peroxides. The writer hopes to be able to publish further results soon.

Recommendations of the Uniform Methods Committee

THE Uniform Methods Committee, composed of N. C. Hamner, chairman, W. H. Irwin, J. J. Vollertsen, and G. W. Agee, made the following recommendations to the American Oil Chemists' Society Convention at New Orleans after the various papers had been read:

1. We recommend the adoption of the Refining Committee report.
2. We recommend the adoption of the report of the Moisture Committee.
3. We recommend that in the determination of free fatty acids in oil extracted from meats or seed, that Phenolthallein be used as the indicator.
4. Reference is made to the report of the Corn Oil Committee; we recommend that this report be accepted as a progress report and referred to the new Committee.
5. Referring to the communication or report from Mr. Thurman of the American Linseed Oil Co., we recommend reference to the Fat Analysis Committee for their consideration.
6. Reference to Committee on Color of Cake and Meal: we recommend adoption of the report.
7. We recommend adoption of the report of the Committee on Color of Oil and suggest further study of this problem.
8. Reference is made to report of the Sampler Committee; we recommend acceptance of this report and suggest that the recommendation regarding certificates is a matter which should be properly acted on by the Rules Committee of the Interstate.