Continuous Vacuum Bleaching of Vegetable Oils[1]

R. R. KING and F. W. WHARTON, Technical Division, Mrs. Tucker's Foods, Inc., Sherman, Texas

ABSTRACT

A continuous vacuum bleaching process which has been in operation on a plant scale for eight years is described, and plant scale results are compared with atmospheric batch bleaching. Advantages of the continuous vacuum bleaching process are shown to be greater color reduction, better stability against oxidation, no free fatty acid rise, greater reduction in soap content, use of less adsorbent, less subsequent catalyst poisoning in hydrogenation, and better flavor stability of subsequently deodorized oils.

No comparison between batch vacuum and continuous vacuum bleaching is presented, but the probable advantages of the continuous process are deducted.

A CONCURRENT PAPER (1) by the same authors on laboratory studies of oxidation effects in adsorption bleaching of vegetable oils has been recently published. This work may be summarized as follows: In bleaching fatty oils an equilibrium exists between two reactions favorable and two unfavorable in respect to color reduction. Adsorption of color and oxidative decrease in color are favorable. Oxidative increase in color and oxidative stabilization against adsorption are unfavorable. Adsorbents are shown to catalyze these oxidative reactions. Under any comparable set of conditions significantly lower colors result when bleaching is carried out under vacuum or in an inert atmosphere. Multiple stage bleaching under atmospheric conditions shows no advantage because of the adverse oxidative effect but may be advantageous under vacuum conditions. Low pH clays respond better than high pH clays to vacuum bleaching with respect to improved color removal and oil stability.

As a result of the beneficial effect of vacuum bleaching observed in the laboratory a vacuum bleaching system was designed and installed in the Sherman, Texas, plant of Mrs. Tucker's Foods inc., in 1940. A continuous rather than batch procedure was adopted because the former was considered to have certain advantages to be discussed later. This plant has been used continuously for the past eight years in continuous vacuum bleaching of soybean and cottonseed oil, and the data herein presented compare results of such processing with atmospheric batch bleaching. No batch vacuum equipment was available.

The improved results of vacuum bleaching depend primarily on the efficiency of deaeration and dehydration of the oil-adsorbent slurry before it is heated to bleaching temperature. This deaeration and dehydration "in the cold" is accomplished much more effectively by applying a flashing principle of gas release in the continuous process than by subjecting large amounts to vacuum as in the batch process.

Principle of Flashing. The conditions necessary to completely deaerate and dehydrate a slurry of refined oil and absorbent cannot be determined because accurate methods of analysis are not available for small quantities of oxygen and moisture in such a mixture. Analogous engineering and laboratory studies on other problems of removal of gases from liquids indicate that the complete removal of oxygen and water vapor from oil-adsorbent slurry is a most difficult one, especially at low temperatures. This makes us feel certain that a flash procedure, in which the slurry is sprayed into a vacuum chamber, would be many times more efficient than merely agitating a large volume of slurry under vacuum as is done in batch vacuum processes.

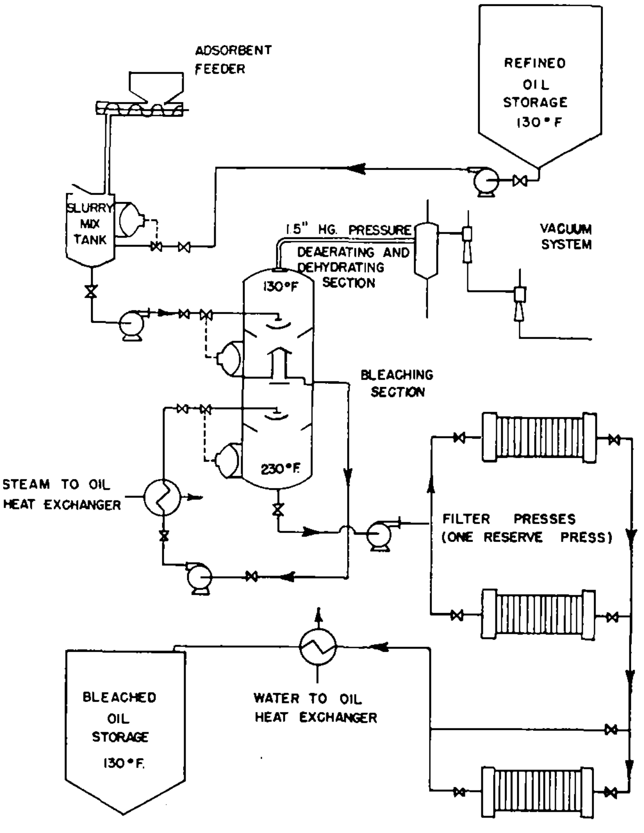

FIG. 1. Continuous vacuum bleaching flow diagram.

The importance of the flash procedure can best be understood by considering numerous examples of the difficulty encountered in removing soluble volatile compounds from oil. The conditions necessary to remove residual solvent from extracted oils by distillation methods is a good example. In laboratory tests 500-gram samples of refined oil containing 1% of hexane were vigorously agitated for 30 minutes at temperature of 220°F. and pressure below 10 mm. Hg. The oils average 0.25% hexane after such treatment. In other tests we have found that at 250°F. it is necessary to steam strip refined oil containing hexane for several hours at pressure below 10 mm. Hg. to eliminate detectable traces of hexane. As another example, it has been observed in the laboratory that volatile material continues to escape from ex-

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TABLE I

Type of Adsorbent Used	pH of Adsorbent	Type of Oil Bleached	Number of Tests Made	Average % of Adsorbent Used		Average Color of Bleached Oil	
				Atm.	Vac.	Atm.	Vac.
Natural Clay 1	6.5	CSO	3	1.27	0.98	2.6	2.4
Natural Clay 1	6.5	SBO	1	1.48	1.46	2.4	3.1
Activated Clay 1	3.6	CSO	2	1.57	1.60	3.0	2.8
Activated Clay 1	3.6	SBO	2	1.55	1.40	5.4	5.2
Activated Clay 2	3.2	CSO	3	1.46	0.90	2.4	2.1
Activated Clay 2	3.2	SBO	1	1.32	1.30	2.4	2.5
Activated Clay 2 plus 4% Carbon	......	SBO	1	0.92	0.92	3.7	2.5
Activated Clay 1 plus Activated Clay 2	......	SBO	1	1.011	0.962	4.2	2.5
General Average (14 Tests)	......	....	....	1.37	1.16	3.2	2.9

pressed refined oil after it is held several hours at temperatures of 250°F. and pressure below 2 mm. Hg. Therefore, it can be concluded that it is quite difficult to remove even low molecular weight, low boiling volatile material from oils by simple evaporation. Furthermore, it is reasonable to assume that it would be even more difficult in a slurry of oil and adsorbent since the adsorbents commonly used in bleaching fatty oils have a strong affinity for gases, water, and probably other volatile material often present in refined oils. The affinity for gases by such adsorbents is illustrated by their use in gas masks.

Mechanics of the Process. A flow sheet of the continuous vacuum bleaching process (2) is shown in Figure 1. Adsorbent material is proportioned continuously, by means of a screw type feeder, into refined oil from storage at an oil temperature of approximately 130°F. The slurry of oil and adsorbent is sprayed into a vacuum chamber through a nozzle impinging upon a baffle plate, thus "flashing off" gases and moisture dissolved in the oil, and adsorbed to the bleaching material. The retention time in this deaeration and dehydration chamber is approximately seven minutes. The slurry is then pumped through a heat exchanger where the temperature is elevated to 220°-240°F. and sprayed into a second chamber where it is retained for approximately 10 minutes. This second flashing into vacuum is for the purpose of removing gaseous products of heat decomposition and "bound" water released by heat. The hot slurry is then pumped through two closed filter presses connected in series and cooled to 150°F. before it is exposed to the air. The deaeration and bleaching chambers are superimposed to conserve space, utilize a single vacuum system, and in general simplify design. The entire system is closed to atmospheric exposure from the time the cold unbleached oil enters the system until the cooled bleached oil is discharged.

Two new continuous vacuum bleaching units are under construction at the present time. These units will be equipped with oil to oil heat exchangers to conserve heating steam and cooling water. The oil-earth slurry will be sprayed into the vacuum chamber through an improved nozzle design without impinging on a baffle plate because it is believed that the advantages gained from the kinetic effect would be more than offset due to coalescence of dispersed droplets at the points of impact. Otherwise design and operation are essentially the same as in the original unit except that aluminum alloy filter presses are used instead of cast iron presses.

Experimental Procedures. A limited number of plant runs were made comparing the continuous vacuum bleaching procedure described above with the following atmospheric procedure. A pre-determined percentage of adsorbent was added to 60,000- to 90,000-pound batches of refined oil in an open kettle equipped with a mechanical agitator. The slurry was heated to 220°-240°F. with agitation and pumped directly through two closed filter presses connected in series. The discharge from the presses was continuously cooled to 160°F. or below by means of a heat exchanger.

In making a single comprehensive plant test, a minimum of 100,000 pounds of oil is required, or 200,000 pounds for a set of comparative tests. Even this quantity is far from sufficient to completely fill a press with spent adsorbent material. The only true plant test requires that the presses be completely filled with spent cake where as much as 250,000 pounds of oil per test is needed. This means that up to 500,000 pounds of oil is needed per single set of comparative runs. Plant experiments, which require one-fourth to one-half million pounds of oil, have to be made at the convenience of the production department, which has definite schedules to meet, and it is very seldom that a set of comparative tests can be made on the same day or even on identical oil. Therefore, in some cases, more accurate information can be obtained by comparing results over long periods of operation using the two different procedures than on the basis of individual plant tests.

Scope of the Data. It is well known in the industry that plant results cannot be duplicated using laboratory bleaching procedures because of the effect of a coated filter press on oil color. In large scale bleaching color is sometimes adsorbed not only due to contact between oil and adsorbent in the bleaching chamber but also due to forcing the oil under pressure through a layer of adsorbent material caked on the press cloths. The effect of this "press bleach" under vacuum versus atmospheric conditions has not been fully investigated, but it is known to occur to an appreciable extent in most cases regardless of the type of plant methods.

Plant bleaching is an extreme example of laboratory studies having limited application to plant conditions. Therefore, if the published scientific literature is to reflect practical aid to industry, deviation from and liberties with the orthodox methods of presenting academic research work must be taken. Since plant conditions in this type of work can rarely ever be controlled to the satisfaction of "pure science," deductions, extrapolations, opinion of experienced observers, coupled with incomplete data, must all be used in some cases to arrive at practical conclusions. Wherever such liberties are taken in this report, they are so indicated.

Effect on Color Reduction. A total of 14 plant tests were made comparing atmospheric batch bleaching with continuous vacuum bleaching procedures. Results are summarized in Table I.

None of these tests were made on the same day, and identical oils were used in only three comparative tests; once on refined cottonseed oil using activated clay 2 and twice on refined soybean oil using a mixture of the two activated clays and activated clay 2 plus 4% of an activated carbon. Results of all three of these tests were in favor of the continuous vacuum bleaching procedure. Although identical oils were not used for the other tests comparing atmospheric batch with continuous vacuum bleaching, the average refined color and official bleach color of the oils used in each method of bleaching was practically the same. Oils used in atmospheric batch bleaching averaged 35 yellow-8.0 red color and 20 yellow-2.6 red official bleach. Oils used in continuous vacuum bleaching averaged 35 yellow-7.8 red color and 20 yellow-2.6 red official bleach.

These data show a definite advantage for continuous vacuum bleaching over atmospheric batch procedures. The advantage is greater when low pH clays are used as the adsorbent.

The oils used in making these tests were refined from mixtures of several tank car shipments of crude oil and were withdrawn from refined oil storage tanks after varying storage periods. Therefore no comparison can be made between the relative efficiency of continuous vacuum bleaching on good and poor quality oils.

Effect on Bleaching Economy. The average of the data from Table I, which represents the bleaching of approximately three million pounds of oil, is interpreted to a common residual color of 3.0 red, by means of adsorption isotherms plotted from laboratory data, and shown in Table II.

TABLE II

	% Adsorbent		Color-Red	
	Atm.	Vac.	Atm.	Vac.
Average data (Table I)	1.37	1.16	3.2	2.9
Interpreted	1.45	1.12	3.0	

These data show a reduction in adsorbent usage of 23% when the continuous vacuum process was used as compared to the atmospheric batch process. As all plant managers know, the main cost saving in reduced earth dosage is not in the cost of the earth itself but in the reduction of the cost of the oil retained in the spent earth.

Effect of Oil Stability. Stability tests were made, using the so-called Swift method, on a composite sample of all of the plant tests previously referred to. Average results are given in Table III.

The average reduction in oil stability was 20% in atmospheric and 7% in continuous vacuum bleaching. This shows an advantage of 13% in favor of the latter procedure. The effect of each of the three types of adsorbent used in the plant tests on Swift Stability is given in Table IV.

TABLE III

Kind of Oil	Atmospheric Batch Bleached		Continuous Vacuum Bleached	
	Stability Ref. Oil	Stability of Bl. Oil	Stability Ref. Oil	Stability of Bl. Oil
	hours	*hours*	*hours*	*hours*
CSO	14.1	11.5	13.4	12.5
SBO	13.2	10.5	13.0	12.0
Average	13.65	11.0	13.2	12.25

It is interesting to note that the natural clay, which responded least to vacuum bleaching in regard to color reduction, also caused the greatest reduction in oil stability. The most likely explanation is that oxygen adsorbed to this clay is more strongly bound than that adsorbed to the activated clays tested.

TABLE IV

Type of Adsorbent Used	pH of Adsorbent	% Reduction in Oil Stability During Bleaching	
		Atmospheric	Continuous Vacuum
Natural Clay	6.5	21	14
Activated Clay 1	3.6	15	4
Activated Clay 2	3.2	25	4

Effect on Free Fatty Acid Rise. Theoretically no free fatty acid rise can occur in bleaching a completely dry oil with a completely dry adsorbent material because no hydrolysis of soap or neutral oil can take place in the absence of moisture. However, some moisture is usually present in refined oils and in the adsorbent materials used for bleaching, and consequently, some hydrolysis usually takes place. Average free fatty acid content of the oils used in these plant tests, before and after bleaching, with each of the three clays in atmospheric and continuous vacuum methods is shown in Table V. The soap content of the unbleached oils used in these tests averaged slightly over 100 parts per million.

TABLE V

Type of Adsorbent Used	pH of Clay	Percentage Free Fatty Acids			
		Original	Atm. Bl.	Original	Vac. Bl.
Natural Clay	6.5	.070	.070	.065	.060
Activated Clay 1	3.6	.063	.073	.117	.113
Activated Clay 2	3.2	.087	.117	.090	.093

These data show there is a significant advantage of continuous vacuum bleaching over atmospheric bleaching from the standpoint of free fatty acid rise in bleaching when low pH value adsorbents are used. It should be observed that no significant increase in fatty acids occurred during continuous vacuum bleaching regardless of pH value of the adsorbent.

Effect on Soap Content. The average soap concentration in oils bleached by the continuous vacuum versus atmospheric batch method is given in Table VI.

TABLE VI

Bleaching Procedure	P.P.M. Soap in Ref. Oil (Avg.)	P.P.M. Soap in Bleached Oil		
		High	Low	Average
Batch Atmospheric	103	55	14	32
Continuous Vacuum	114	20	3	15

These data show that continuous vacuum bleaching is decidedly beneficial in regard to soap removal from refined oils. This benefit is no doubt due to superior dehydration of the oil and adsorbent. A completely dehydrated soap is insoluble in oil whereas a hydrated soap appears to be somewhat soluble even in a dry oil.

Effect on Hydrogenation Catalyst. Since soap is a catalyst poison, it would be expected that vacuum bleaching would increase the active life of nickel catalyst used in hydrogenation of bleached oils. This is shown to be true from studies of catalyst usage for a period of several months in which a continuous atmospheric system was used for bleaching versus a similar period after the continuous vacuum system was put in operation. The quantity of catalyst consumed per unit weight of oil hardened to a definite iodine value reduction and, maintaining the same rigid manufacturing standards as to selectivity, was approximately 25% less on the vacuum bleached oil. There is little doubt that this benefit is due principally to soap removal, but it may be due in part to improved oil stability.

Effect on Flavor Stability. Since oxidation of the oil during bleaching is significantly reduced and the stability of the bleached oil to subsequent oxidation is significantly improved in vacuum bleaching, it seems almost certain that some improvement in flavor characteristic of the subsequently processed bleached oil should result. We are rather well convinced that continuous vacuum bleaching improves flavor and flavor stability of deodorized oils to a marked extent. This opinion is, however, based more on comparison between deodorized oil quality before and after the continuous vacuum system was put in operation than on results of individual tests. Oil flavor is such a nebulous characteristic that a reasonably accurate opinion can be formed only after accumulation of a relatively large amount of data and experience.

Only two comparisons have been made under controlled conditions between identical oils atmospherically batch bleached versus continuous vacuum bleached, in which the oils were kept separate through hydrogenation and/or deodorization. These tests were made on a refined soybean oil, and the same percentage of an activated clay was used in both bleaching procedures. The vacuum bleached oils, both unhardened and hydrogenated, were decidedly superior to the corresponding atmospherically bleached oils in flavor stability after deodorization.

A limited number of tests have been made in our own and other laboratories comparing plant processed samples of continuous vacuum bleached oil with identical oil open kettle bleached. On these samples subsequent hydrogenation and deodorization was done in the various laboratories. Results of some of these tests showed the vacuum bleached oil to be decidedly superior. Other tests showed no significant difference. Results are inconclusive but are in favor of vacuum bleached oil.

Batch Vacuum Versus Continuous Vacuum Bleaching. Since no plant equipment for batch vacuum bleaching was available, no direct comparisons could be made of continuous versus batch vacuum bleaching. However, it is reasonable to deduct that the continuous process would have the following advantages over batch vacuum procedures for large scale bleaching although the magnitude of the difference is not known:

1. More complete deaeration and moisture removal because the oil-adsorbent mixture is flashed into a vacuum chamber below bleaching temperature.

2. The contact time between oil and adsorbent is greatly reduced and the effect of residual oxygen on oxidation of the coloring matter is minimized.

3. The bleaching operation can be much more closely controlled, probably affecting economy of bleaching. The quantity of adsorbent may be increased or decreased at any time during operation, to adjust and maintain a desired color effluent with a minimum of adsorbent.

Summary

A continuous vacuum bleaching method which has been in operation on a commercial scale for a number of years is described. The fundamental principles in this process are:

1. Deaeration and dehydration of the oil-adsorbent mixture in the cold by continuously flashing the slurry into a vacuum to remove moisture and oxygen prior to bleaching.
2. Further dehydration and degasification after heating to bleaching temperature by continuous flashing into a vacuum to remove bound water and gaseous products of decomposition.
3. Maintaining a closed system throughout the process to avoid atmospheric contact from the time the cold refined oil enters to the time the cooled bleached oil leaves the system.

This process is shown to have the following advantages over atmospheric open kettle bleaching:

1. Lower bleached oil colors.
2. A more stable oil to oxidation and flavor reversion.
3. Free fatty acid rise in bleaching is eliminated.
4. A greater reduction in soap content in oil.
4. Use of less adsorbent.
6. Less subsequent catalyst poisoning in hydrogenation.
7. Better flavor stability of subsequently hydrogenated and deodorized oils.

Although direct comparisons were not made between batch vacuum bleaching and continuous vacuum bleaching, it is deducted that the above advantages would be apparent for vacuum bleaching continuously although probably not of as a great a magnitude.

REFERENCES

1. King, R. R., and Wharton, F. W., J.A.O.C.S. *26*, 6 (1949). "Oxidation Effects in Adsorption Bleaching of Vegetable Oils (1949).

2. U. S. Patent 2,428,082, September 30, 1947, R. R. King, S. E. Pack, and F. W. Wharton.