SYMPOSIUM: PROCESSING OF EDIBLE OILS

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Clay-Heat Refining of Edible Oils[1]

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ABSTRACT

The treatment of crude edible oils with sodium hydroxide solutions is the standard refining procedure in the industry. Refining with NaOH removes free fatty acids, some phosphatides, proteinaceous matter and some colored material. Up to now experience has shown that most oils cannot be deodorized satisfactorily unless they have been caustic-refined. In the past, when most crude oils contained several per cent of free fatty acids, caustic-refining offered itself as a particularly suitable means of preparation for further processing. In recent years the free fatty acid content of crude oils has been, in most cases, only a fraction of 1%, which could very readily be removed in the process of deodorization. A prerequisite for this would be to remove by some other means those substances that interfere with satisfactory deodorizing. It has been found that the process of bleaching can be used for this purpose if the oil is pretreated with 0.1-0.5% phosphoric acid and bleached at 325-350 F. The amount of bleaching clay required depends on the type of oil and its quality, but with many oils up to 2% clay is satisfactory. The amount of phosphoric acid necessary also depends on the type of oil.

INTRODUCTION

The most important and widely practiced method of refining is the treatment of crude oils with an alkali. Alkali-refining removes free fatty acids and other acidic materials, and there is some removal of phosphatides, proteinaceous matter and color. Up to now experience has shown that most oils cannot be deodorized satisfactorily unless they have been alkali-refined.

In the past, when it was usual for most crude oils to contain several per cent of free fatty acids, alkali-refining offered itself as a particularly suitable means of preparing oils for further processing. In recent years the free fatty acid content of the most heavily used crude oils in the U.S. and Canada, soybean oil and rapeseed oil, has been in most cases only a fraction of 1% which could be readily removed in the process of deodorization. A prerequisite for this would be to remove by some means other than alkali-refining those substances which interfere with satisfactory deodorizing.

The patent literature contains a number of references to processes which claim to achieve this. Thus Bock et al. (1) contact the oil with small amounts of mineral acids or their salts, or organic acids and their anhydrides. The "refining" agent must be introduced into the oil by first mixing it with an emulsifying agent such as the well known mono- and diglycerides. Bleaching clay (at 212 F), charcoal or filter-aids are used to remove the "refining" agent together with the impurities. Alternatively, centrifugation or decanting is used. The oils are then subjected to deodorization.

Sullivan and coworkers (2) use a heat treatment above 400 F in which careful temperature control is exercised. This is said to precipitate, as well as pyrolyze, the oil soluble constituents that seem to interfere with the deodorizing process. Careful control of the cooling rate of the oil is necessary to avoid re-solution of the materials to be removed. No bleaching clay or other absorbent is used. Coagulated material is removed by centrifuging, settling or filtering. In some cases washing with water or with alkali solutions is necessary to achieve color stability during deodorization. Kelley (3) contacts cottonseed oil with 5-10% water at 115 F and then bleaches with acid-activated clay at 220 F. The bleached oil is deodorized and claimed to be of good color and bland flavor.

It is of course well known that oils such as lard, tallow and palm oil, and perhaps to a lesser extent coconut oil, can be processed to deodorized oil products of good quality without alkali-refining. Often these oils are merely bleached

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[1] One of nine papers presented in the symposium "Processing of Edible Oils," AOCS Meeting, Ottawa, September 1972.

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and then deodorized.

In the course of some experimentation with bleaching clay to remove catalyst poisons from oils, the possibility arose of modifying the process of bleaching to enable treatment of the entire range of oils usually processed in refineries without alkali-refining.

EXPERIMENTAL PROCEDURES, RESULTS AND DISCUSSION

Clay-Heat Refining of Various Oils

Preliminary tests with acid-activated bleaching clay (Special Filtrol 4) and earlier observations indicated that bleaching at temperatures of 450-500 F under nitrogen or vacuum gave oils of good color and of good initial flavor and flavor stability. The oils used were soybean, rapeseed and a herring oil hydrogenated in the crude. Further tests showed that pretreating crude, degummed soybean oil at room temperature with 0.1% concentrated phosphoric acid made it possible to reduce the bleaching temperature to 340 F and still achieve good results. A variety of crude oils were tested to determine if the process outlined above would result in deodorization of these oils to a satisfactory flavor, color and stability. In detail, the apparatus and procedures were as follows: 1000 g crude oil was weighed into a 2000 ml three-neck distillation flask fitted with a thermometer, a variable speed agitator and a glass tube connnected to a nitrogen supply. The oil in the flask was heated to 100 F with an electric heating mantle. Concentrated phosphoric acid was pipetted into the oil and the mixture agitated at slow speed for 15 min. Next, bleaching clay and filter-aid were added and a stream of nitrogen was bubbled through the mixture. Heating of the mixture was continued to 350 F. During heating the neck of the flask was kept hot to avoid moisture condensation. As soon as the maximum temperature was reached the heating mantle was removed and the flask cooled to 230 F. The cooled oil was then filtered and deodorized.

In order to establish the amounts of phosphoric acid and bleaching clay that would be required, a series of preliminary tests were done with a small quantity of each of the oils.

Table I lists the oils treated and the amounts of phosphoric acid, bleaching clay and filter-aid used with each. After the refining treatment the oils were analyzed for color and free fatty acid content, and after deodorizing, for color, free fatty acids, flavor, AOM and Schaal oven stability (at 115 F).

Table I indicates that good colors are being achieved after clay-heat refining, except for cotton oil which went black even though 6.0% clay and 0.3% phosphoric acid were used on it. Preliminary tests had already indicated that quite unreasonable amounts of bleaching clay would be required to achieve satisfactory results. Corn oil also required 6.0% bleaching clay and 1.0% phosphoric acid, but then gave a satisfactory quality oil.

Deodorized oil colors are satisfactory in all cases. The flavors are also satisfactory, except in the case of the expeller rapeseed oil which was not quite bland. It should be noted that a perfectly bland oil is sometimes difficult to achieve with some lots of oil, even after alkali-refining. Tallow, which is not included, may be expected to behave similarly to lard. The stability of the various oils compares well with that obtained from caustic-refined oils.

It is evident that the amount of clay and phosphoric acid required may vary widely, depending on the type of oil to be treated. Apart from the extreme of corn oil, clay amounts of 1.5-4.0% and phosphoric acid amounts of 0.1-0.4% are indicated. It should be kept in mind, however, that the amounts used in these tests were designed to *ensure complete removal of impurities. Minimizing oil*

TABLE I

Clay-Heat Refining of Various Crude Oils

Analysis	Soybean	Expeller rapeseed	Sunflower	Corn	Peanut	Palm	Coconut	Palm kernel	Seal	Dry rendered lard	Cotton
Crude free fatty acids, %	0.30	0.31	0.28	2.35	1.07	3.55	1.23	6.40	1.46	0.34[a]	
Treatment active clay, %	2.0	4.0	1.5	6.0	4.0	4.0	2.0	2.0	4.0	2.0	6.0
Filter-aid, %	0.5	1.0	0.4	1.5	1.0	1.0	0.5	0.5	1.0	0.5	1.5
Phosphoric acid, %	0.1	0.4	0.2	1.0	0.2	0.4	0.1	0.1	0.2	0.3	0.3
Temperature, F	350	350	350	350	350	350	350	350	350	350	350
Treated oil color, red	1.0	1.3	0.4	2.0	0.9	1.4	0.4	0.7	...[b]	0.5	Black
Free fatty acids, %	0.73	0.36	0.45	2.67	1.28	3.89	1.53	7.3	...	0.48	
Deodorized oil color, red	0.7	1.0	0.4	2.0	0.7	1.7	0.7	0.7	1.3	0.6	
Free fatty acids, %	0.03	0.02	0.02	0.03	0.02	0.03	0.02	0.03	0.03	0.03	
Flavor	Bland	Good	Bland	Bland	Bland	Bland	Bland	Bland	Bland	Bland	
AOM, hr	6	18	9	13	18	>60	>60	>60	25	4	
Schaal, days	11	12	15	8	17	15	>30	20	8	5	

[a] Crude oil color very poor (9. OR).

[b] Directly hydrogenated to 76 IV.

TABLE II

Tocopherols and Conjugation

Analysis	Crude soybean oil	Caustic-refined oil: Refined	Caustic-refined oil: Refined, bleached	Clay-heat refined oil
Free fatty acids, %	0.68	0.03	0.04	0.90
Color (red)	---	9.5	1.8	1.1
Peroxide value, me/kg	3.0	3.5	2.0	0
Tocopherols, %	0.148	0.138	0.126	0.136
Conjugated diene, %	0	0	0	0
Conjugated triene, %	0.003	0.002	0.043	0.054

losses was not a major consideration. It is conceivable that some clay or some acid usages were higher than necessary.

Tocopherols and Conjugation

Some test work was also done to establish whether clay-heat refined oils would be significantly different from caustic-refined oils with respect to tocopherol content and degree of conjugation. Total tocopherol content does not appear to be significantly affected under ordinary bleaching conditions, but under these rather severe conditions this could be changed. Some conjugation does take place during commercial bleaching of oils such as soybean, corn and cotton, and under clay-heat refining conditions this could be more severe.

Crude soybean oil was used for the comparison. The clay-heat refining was done using 0.2% phosphoric acid and 2.0% Special Filtrol 4 at a maximum temperature of 360 F. Caustic-refining was done in the plant in continuous refining equipment, followed by bleaching in the laboratory with 1% Special Filtrol 4.

The results, including pertinent data on the crude oil used, are listed in Table II.

The data in Table II indicate a reduction of tocopherols from 0.148% to 0.138% during caustic-refining, and a further reduction to 0.126% during bleaching. These two losses are roughly equal in magnitude. Clay-heat refining reduces tocopherol to 0.136%, about the same loss as in either refining or in bleaching. Thus only about one half as much tocopherol is lost in clay-heat refining as in caustic-refining followed by bleaching. Conjugated trienes increased during bleaching, as would be expected, and there is also an increase during clay-heat refining. This latter increase is slightly larger than in ordinary bleaching.

Clay-Heat Refining with Various Bleaching Clays

Samples of different bleaching clays from a variety of suppliers were evaluated for their effect on the clay-heat refining of crude soybean oil. The tests were done under a vacuum of 29 in. Hg, using 0.1% concentrated phosphoric acid, 1.0% clay and a maximum temperature of 350 F. Holdup time with the acid in the oil was 15 min at 100 F, and 20 min at 350 F with the clay added. In addition to determining if the clay had effectively "refined" the oil, the color achieved with each clay was also recorded. Table III lists the various clays and the results.

TABLE III

Clay-heat Refining with Various Bleaching Clays

Clay	Refining comments	Oil color, red
BC 300	Not refined	0.5
BC 200	Not refined	0.8
Vega Plus	Refined	1.0
Filtrol 105	Refined	1.1
SK 385	Refined	1.1
Tonsil IFF	Not refined	1.1
Vega 1	Not refined	1.1
Vega 4	Refined	1.1
Vega 5	Not refined	1.1
Impact 150	Refined	1.2
Filtrol Spec. 4	Refined	1.3
Supact 150	Refined	1.5
Vega 105	Refined	2.2
Vega 6	Not refined	2.2
Filtrol 20	Refined	2.2
Filtrol 13	Refined	2.6
BCX	Not refined	3.1
BC Natural	Not refined	4.2

Table III shows that only some of the clays are suitable for clay-heat refining under the conditions used. All of the ones that perform satisfactorily are acid-activated; the two natural clays, BCX and BC Natural, are not suitable. It is surprising that some clays are not effective, since it might be assumed that clays suitable for oil bleaching would also be suitable for clay-heat refining. Presumably, differences in the adsorptive properties of the various clays are responsible for the different behavior.

It is also interesting to note the considerable differences between clays in the amount of color removed from oil in the process. The clays are listed in the order of their bleaching effect, and it is obvious that their usefulness in clay-heat refining is not dependent on their bleaching

TABLE IV

Various Acids in Clay-Heat Refining

Acid	Amount used, %	Clay used, %	Maximum temperature, F	Oil color, red	Deodorized oil: Color, red	Deodorized oil: Flavor
Phosphoric	0.1	1.0	340	1.8	---	---
Hydrochloric	0.1	1.0	390	4.5 (off)	---	---
Sulphuric	0.1	1.0	340	Black	---	---
Nitric	0.1	1.0	390	Dark brown	---	---
Acetic	0.1	1.0	390	5.2 (off)	---	---
Citric	0.2	2.0	350	1.4	0.6	Acceptable
Boric	0.2	2.0	350	1.3	1.2 (off)	Poor
Phosphoric	0.1	2.0	350	1.4	0.6	Acceptable
None	—	2.0	350	1.2	1.6 (off)	Very poor

properties.

Various Acids in Clay-Heat Refining

As mentioned earlier, the usefulness of phosphoric acid in clay-heat refining lies in the fact that temperatures of ca. 350 F rather than 450 F can be used. Additional tests were done to investigate whether other acids would be similarly effective. The acids considered are the various common mineral acids, and acetic, citric and boric acids. Crystalline citric and boric acid were used; all others were used as the liquid, concentrated, commercial acid. The test oil was again crude soybean oil. The acid pretreatments were carried out at 80 F for 30 min followed by clay additions and further heating as indicated in detail in Table IV. Special Filtrol 4 clay was used.

The results of the various acid pretreatments in Table IV indicate that among the mineral acids only phosphoric acid gives oil of satisfactory color and flavor. Hydrochloric, sulphuric and nitric acid are not suitable because off-colors are produced, particularly with sulphuric and nitric acids. Among the organic acids only citric acid gives satisfactory results. With oils that have a tendency to foam, phosphoric acid would be preferred since it effectively suppresses foaming, whereas citric acid does not.

REFERENCES

1. Bock, H., and H. Hommers, U.S. Patent 3,354,188 (1967).
2. Sullivan, F.M., U.S. Patent 2,441,923 (1948).
3. Kelley, W., U.S. Patent 1,747,675 (1930).

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