Bleaching Practices in Europe

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ABSTRACT

Adsorption onto porous solids is used to remove from oils not only pigments but also several other minor components. Now that long established process steps such as degumming, neutralization, and washing have become even more effective, the technique of adsorption is being continually evaluated to ensure that no unjustified expenditure is allowed to continue. Practical advice is offered on bleaching procedures and the subsequent separation of the adsorbent from the oil.

INTRODUCTION

Bleaching is popularly and correctly regarded as the partial or complete removal of color. The application of heat to oil can destroy the pigment, as in the case of carotene in palm oil. On the other hand, heat, especially in the presence of air, may encourage the production of colored degradation products such as chroman 5, 6 quinone from the γ-tocopherol present in many oils, and these may stubbornly resist further attempts to remove them (1,2). Heat is therefore restricted to particular applications and used with discretion.

Chemical attack on the pigment via oxidizing agents will involve the triglyceride molecules also; this may be acceptable where the oil is being used for technical purposes such as soapmaking, but the risk of generating off-flavors or their precursors cannot be accepted for edible products. There remains the important and long established technique of adsorbing pigment onto natural or activated earth or carbon where at least part of it may be removed or destroyed. It must be emphasized that several other materials compete with pigments for space on the adsorbent surface. Indeed, frequently there are circumstances in which the oil refiner is primarily concerned with the removal of these non-pigment materials since the oil is already sufficiently light in color or because the color will be considerably diminished in a subsequent process step such as hydrogenation or deodorization. Important non-pigments are residues of soap which would hinder filtration or later generate an off-flavor; gums, including phosphatides and related substances which above a certain level are associated with flavor instability; and traces of pro-oxidant metals arising from their previous use as catalysts or simply contamination from tanks, vessels, and pipelines. Many refiners see an advantage in the destruction of lipid peroxides and the possible adsorption, in part at least, of their breakdown products at the bleaching stage, especially when an activated earth is used.

These are the circumstances in which "bleaching" becomes too narrow a description; "adsorptive cleansing" would be more accurate. When this concept is accepted, it becomes easy to understand why the need for such a step has come under increasingly critical evaluation. Degumming, neutralization, and washing techniques which remove mucilage and soap to very low levels by use of centrifuges are now widespread and facilitate reduction in the amount of earth used or in the most favorable circumstances to its omission. Control of the quality of some crude oils is also becoming more effective. Reduced earth usage means reductions in earth cost, oil lost in earth, and solid effluent and increased filter utilization.

Even so, earth treatment remains an important part of the processing of many oils. It is the aim of this paper to indicate the conditions in which it is most effective and economical. Finally, advice is given on the separation of the earth from oil.

BLEACHING EARTHS AND CARBONS

Natural Bleaching Earths

Prolonged weathering has leached some of the aluminum ions from the complex silicates which constitute the bulk of natural bleaching earths, and these also contain various proportions of Mg, Ca, Na, and Fe. Molecular lattice structure, macropore structure, and particle size all affect the capacity to adsorb water, oil, phosphatides, soap, color bodies, and metals. The best earths are reported (3) as capable of adsorbing from suitably strong solutions of pigment up to 15% of their own wt of such pigment; in everyday use, they easily retain about 30% of their own wt of oil. They are employed to remove or greatly diminish traces of soap (present at up to 500 ppm); they are cheap and do not elevate FFA or isomerize unsaturated fatty acid groups. They are commonly employed for the decolorization of easily bleached oils such as washed cottonseed, coconut, lard, top edible grade tallow, and hardened oils. For heavier duties, prohibitive doses would be necessary; hence, activated earths are then employed.

Activated Bleaching Earths

Certain inactive clays or earths (nonswelling sub-

TABLE I

Typical Characteristics of Adsorbents

	Natural earth	Activated earth	Activated carbon
pH (suspension in water)	8.0	2.8-6.0	6.0-10.0
Apparent bulk density (g/ml)	0.68-0.90	0.32-0.68	0.38-0.43
Surface area (m^2/g)	68	165-310	500-900
Particle size (microns) distribution	%	%	%
above 80	19	10-15	
40-80	20	20-25	
above 50			30-10
20-40	19	25-30	
10-50			40-50
under 20	42	30-40	
under 10			30-40

betonites), when extracted to varying degrees with sulphuric or hydrochloric acid, washed, dried, and milled, exhibit different degrees of acidity, power of adsorption, and particle size distribution.

The chemical state of the pore surface has been so changed that it acts as a modified ion exchange medium. Naturally, the acid extraction has greatly increased the void spaces in the particles as well as total surface area; hence, the earth may retain up to 70% of its own wt of oil. Such earths are more likely to split soap residues and hence elevate FFA, destroy peroxides, and promote isomerization. The latter effect is, however, more obvious above 150 C, which is of course well above the temperatures (90-110 C) at which most oils are earth bleached. These earths will readily take up soap, gums, etc., but are especially useful in treating the less easily bleached oils such as palm, castor, inedible tallow, linseed, soybean, and rapeseed, or where removal of trace metals and phosphatides is more important than rise in FFA, which in any case is destined to be removed at a subsequent stage.

Activated Carbon

Tar is removed from the pores of incompletely combusted wood by preferential oxidation, steam, or acid. Washing, drying, and grinding gives a well ordered range of activated carbons with various pore sizes, internal specific surface areas, and residual acidity or alkalinity. Since the relation between the size and shape of the pores and the size and shape of molecules they are intended to adsorb is of crucial importance, efficiency must be evaluated in the same context as that in which it is proposed the carbon should be used. Not only the large specific surface but also its chemical state determines the activity. Up to 150% of its wt of oil can be retained by an activated carbon. Carbon is more expensive than earth; also by a form of synergism the best decolorization may well be obtained by a 40:60 carbon-earth mixture. If a slightly higher color than that achievable by such a mixture is acceptable, a 10:90 carbon-earth mixture will be more economical. Five ringed polycyclic aromatic hydrocarbons which are not volatilized by deodorization can be satisfactorily adsorbed by up to 0.4% doses of the best activated carbon. These hydrocarbons are only likely to be present in appreciable amounts if the oil seed has been directly exposed to flue gases in drying (4).

Temperature

With nearly all edible oils, bleaching earths are used at 90-110 C. Low temperatures probably favor the retention of the adsorbed pigment on easily accessible surfaces; higher temperatures (above 100 C) favor movement into capillaries where chemisorption is most likely. Above 95 C the splitting of soap to fatty acid is more obvious with acid activated earths. At 160 C structural changes in unsaturated fatty acid groups become increasingly probable.

Time

In batch equipment operating gate type stirrers at about 40 rpm, adsorption will be virtually complete within 15 min. Since the oil waits to pass through a filter, this contact time is usually appreciably exceeded. With continuous neutralizing, washing, and drying equipment it is possible to dose the earth into the oil with brisk agitation in a small vessel and pump immediately to the filter: total contact time about 5 min. This seems to work well when the earth is primarily expected to remove traces of soap and mucilage before the oil passes to another stage such as hydrogenation.

Moisture

Usually oil is dried under vacuum to $<0.2\%$ moisture. Earth stored in a European climate will not generally exceed 10% moisture content. Abnormally moist earth added to hot oil (ca. 100 C) causes frothing; wet oil (0.3% moisture) leads to filtration difficulties and delay.

Air Contact

Because oxidation may fix some colors while removing others and is in any case likely to damage flavor stability, contact with air during and after bleaching and prior to deodorization should be minimal. Vacuum is commonly applied during bleaching but, with batch equipment at least, is commonly broken by air prior to filtration.

Earth Dosage

The efficiency of an adsorbent is measured by the minimum dose required to reduce the concentration of adsorbate (pigment or other substances) to the required level. The relative efficiencies of adsorbents may alter or even reverse, depending on the type of pigment involved, and further, even with the same pigment, the relative overall efficiency of two adsorbents may alter or reverse depending on how far the reduction in color is to be taken (5). Having said this, it is nonetheless evident that refiners are able to work satisfactorily with a smaller variety of bleaching earths than was formerly considered desirable. Most edible oils passing through a refinery can be adequately treated when only two earths are held in stock—say, one cheap natural (nonactivated) earth and one moderately activated one (e.g., pH of 10% suspension in water about 4; apparent bulk density, 0.5-0.7 g/ml). A small stock of a particularly highly acid-activated earth (e.g., pH of 10% suspension in water about 3; apparent bulk density 0.4 g/ml) may be held if oils more difficult to bleach are expected. The minimum dose is that required to take up the traces of soap and mucilage which may have escaped earlier process steps, and this will be 0.2-0.4% earth-oil depending both on the condition of the oil and the activity of the earth. Maximum doses range from 1.5 to 2.0% earth.

Procedure

At the moment of addition of earth to oil, the less the air entrained the less the oxidation. How significant this is in flavor terms depends on the kind of oil being handled, so the degree of risk will also vary widely. Even if earth is held under nitrogen prior to dosing, the small volume of air occluded in the pores will persist; this amount will be vastly less than the volume of air drawn through the oil if compressed air or vacuum/suction followed by air is used to move the earth to the bleach equipment.

Since bleaching diminishes the natural antioxidants, if any, in the oil and decomposes peroxides already formed to give conjugated unsaturated fatty acid groups, it is foolish to allow air ready access to the bleached oil, which probably is filtered at around 90 C and is then most vulnerable. For example, a detailed check (6) on the rate at which soybean oil oxidized at different stages of processing led to the conclusion that the storage of bleached oil should be minimized and that storage in the crude state was much safer.

Stirring the contents of a batch bleacher during the 40-80 min of filtration need only be occasional and at most of about 30 sec duration. As the filter cake increases in thickness, the time taken by the oil to traverse it reaches 1-2 min; during this time the concentration of earth in oil is about 70%: useful further bleaching occurs ("press bleaching effect"). Some refiners allow for this effect by decreasing the dose of earth to oil ready to be filtered on a partly filled filter by up to 50% of the initial dose. This increases the utilization of the filter unit and economizes in earth and hence oil lost to earth. If a small dose of citric acid (up to 0.1%) is added to oil about to be bleached, this splits remaining traces of soap and sequesters pro-oxidant metal ions, allowing them to be taken up more effectively by the earth. Although technically logical, pumping neutralized oil through a filled filter prior to adding fresh earth (countercurrent effect [7]) is not generally practiced—possibly because of the extra equipment and manipulation involved. It may be advantageous to add earth in two steps (separated by about 10 min in batch procedures). The first, being a cheap nonactivated earth, will take up the easily adsorbed impurities such as soap; then the second more expensive activated earth takes up pigment and mucilage. The extent to which this is practiced will depend on the oil being handled. If washing after neutralization has been very effective, the advantages will be less. These are considered to be: lower rise in FFA of the bleached oil, possible improved keepability, lower residual oil in filter cake, and reduced earth cost.

Separate continuous bleaching units are available and operated under automatic control. Normally, on entering the top compartment, oil flows over the inner wall of a heated jacket and moisture flashes off under vacuum; citric acid may be added at this point.

At selected intervals—the minimum being about 10 min—the oil is dropped to a middle compartment still under vacuum and with agitation. A measured dose—or series of doses—of earth is added rapidly by an automatic earth dispenser. After the same interval, the oil-earth slurry is dropped to the bottom compartment, which has a greater capacity than either of the others, and it is from here that it is pumped continuously to a filter. These units are flexible, effective, and operate for long periods with a minimum of attention.

Filtration

Filter presses are still widely used, although for new installations semiautomatic versions which eliminate heavy manual work and reduce the number of operating personnel by at least 1/2 are popular. Preshrunk heavy duty cotton cloths are being replaced to an increasing extent by cotton-polyamide or all polyester cloths. Cloths containing synthetic fibers have been woven so that they permit high flow rates combined with good retentivity of solid particles. They are particularly durable and favor easy clean discharge of cake. The life of a polyester cloth can be 5 times that of cotton cloth. The double shrunk twill weave 680 g/m^2 all cotton cloth is likely to be replaced by a twill weave staple fiber 680 g/m^2 polyester cloth with a water permeability of about 3m^2/m^2/min at 25 mm WG. For those who have been accustomed to use a paper overlay, these may often be advantageously replaced by a light closely woven polyester cloth overlay of about 240 g/m^2 (multi-filament plain weave) and similarly low permeability of about 3m^3/m^2/min at 25 mm WG. In the latter case, the wt of the main backing cloth may then be dropped to some 540 g/m^2 and a permeability of about 9 m^3/m^2/min at 25 mm WG accepted. In the above circumstances, there should be no difficulty in maintaining a filtration rate of 200 kg oil/m^2/hr.

Completely enclosed automatic self cleaning filter units are now popular for earth-oil separation as in many other applications. With the bleaching earth particle size distribution which has been normal in Europe as late as 1973, the wire gauze filter element classed as 60-80 microns aperture size represents the best choice. The classic plain Dutch or Hollander weave 24 x 110 (warp: weft per inch) is suitable, or the very similar panzer tressengewebe in which the weft is the thicker. Wire diameters must be chosen by the weaver so that the 60-80 micron aperture is retained. These automatic filters can be provided either in a form where the filter cake is spun off the rotating leaves by centrifugal force alone as a solid discharge, or where a minimum of water is pumped as a reverse flow through the rotating gauzes to help expell the cake as a slurry. This action helps to keep these specially robust gauzes free from fouling but, on the other hand, the disposal of solid effluents is less troublesome in most places. The gauzes must be kept clean to maintain a good filtration rate of 350 kg oil/m^2/hr. Unusually rapid buildup of internal pressure during filtration to the maximum recommended (about 5 atms) indicates fouling of the gauze. As the need arises, one method of cleaning especially applicable to the solid discharge type is to circulate a dilute (0.25N) caustic soda solution forwards, drain, and then pass once in the reverse direction a clean water wash through the gauze. If a reverse wash is employed, it is essential not to exceed the pressure underneath the gauze which the manufacturer recommends as a maximum, and this is likely to be around 0.75 atms in the solid discharge type.

Oil Recovery

When hot (95 C) water is pumped through the cake while maintaining a pressure of 5 atms and hence a rapid flow rate, between 55-70% of the oil content is displaced and separates in a collecting tank from the bottom of which hot water can be recirculated if desired. Washing time is up to 30 min; ratio of wash circulated through the cake to the wt of cake varies from 5:1 to 20:1, the normal being 10:1. About 90% of the oil displaced is obtained in the first 10 min.

After washing, the cake may be partly dried by steaming or air blowing, except hot air is not recommended where highly unsaturated oils such as fish or linseed are involved.

The enclosed automatic filters lend themselves to in situ extraction of the oil with an organic solvent such as hexane, or the oily cake, consolidated by brief nitrogen blowing, may be discharged and extracted in a separate unit. Solvent extraction gives over 95% yield of recovered oil whose quality is quite comparable with the filtered oil itself. The cost of solvent extraction and solvent recovery is so much higher than the less efficient hot water extraction that it can only be contemplated for large refineries, and even here it is the advantage of having a solid effluent with very low fat content that may be the deciding factor.

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