Some Fundamental Aspects of Bleaching[1]

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Abstract

This paper reviews several aspects of bleaching fats and oils. Bleaching is a relatively simple operation from a mechanical standpoint, however the underlying technical background of the reactions occurring in the oil is quite involved and frequently weird, and apparently inconsistent effects result. Specifically, the subjects covered are: (a) effect of bleaching upon the organic peroxides of the oil; (b) nature of the bleaching reaction; (c) variation of bleaching efficiency between clays upon different oils; and (d) filtration factors.

Effect of Bleaching Upon the Organic Peroxides of the Oil

The organic peroxides are formed during the progressive chain of oxidative reactions that occur when oil is stored in contact with air, and ultimately result in rancidity. A positive peroxide test on an oil therefore indicates it is on its way to becoming rancid.

Bleaching to a normal color level reduces the peroxides, and the comparative peroxide reduction achieved by two clays is directly proportional to their respective bleaching efficiencies. Bleaching efficiency of a clay is defined as the per cent of a standard clay required to bleach to a specified color times 100, divided by the per cent of the clay to bleach to that color. When normal quality oil, bleached to normal color level, is stored at room temperature, the peroxide builds up again at a fairly uniform rate, and (a) at approximately the same rate for different clays, regardless of type; (b) at approximately the same rate as on the refined oil.

Table I illustrates the effect of bleaching refined soybean oil upon the peroxides when using different clay types.

Nature of the Bleaching Reaction

When stored at an elevated temperature (220 F), vegetable oil and animal fat usually lighten in color at first, due to oxidative fading of the color pigments, in particular the carotenoid type. The fading progresses to a low level, then the oil darkens as new color is formed by continuing oxidation. At the point of upswing, the oil has become rancid.

The initial reduction in color suggests the possibility that bleaching may be at least partially a matter of color fading with the clay acting as an oxidation catalyst instead of being 100% color adsorption by the clay, the generally accepted theory. However, a simple test demonstrated that bleaching was predominantly an adsorption effect.

Palm oil, rich in carotenoid pigments and hence subject to pronounced fading at an elevated temperature, was bleached, filtered through a Buchner funnel, and the filter cake extracted with solvent (50% acetone/50% benzene). The volume of solvent containing the color as solute was adjusted to that of the unbleached oil with fresh solvent, and read for color.

[1] Presented at the AOCS meeting in New Orleans, April 1970.

TABLE I

Effect of Bleaching Refined Soybean Oil Upon the Peroxides[a]

Clay, %	Natural clay		Activated clay	
	Color Y-R	Peroxides me/kg	Color Y-R	Peroxides me/kg
½	54–7.4	9.9	54–5.3	5.7
1	35–5.2	7.9	27–2.0	2.0
2	25–2.3	5.4	16–1.1	0.9

[a] Refined oil: color 70–8.8, peroxides 6.5 me/kg.

TABLE II

Adsorptive Capacity Natural vs. Activated Clay on Soybean and Palm Oils[a]

Clay	Soybean oil	Palm oil
Natural	4.7	29.1
Activated	8.0	92.6
Adsorptive capacity, % natural vs. activated	59	31
Bleaching efficiency, % natural vs. activated (at 3.0 red)	45	<20

[a] Expressed as lov. red units (5¼ in.) per per cent clay.

This was closely equal to the unbleached oil color minus that of the bleached oil, from which it was concluded the decolorizing must have been due mostly to adsorption by the clay rather than to oxidative fading. Had fading occurred to any extent, it is reasonable to expect the reconstituted color would have been somewhat lower.

Futher, the relative ease by which the color was extracted from the filter cake (by agitation in a few minutes at room temperature) suggests that adsorption is a physical rather than a chemical action between the clay particle and color pigment.

Variation of Bleaching Efficiency Between Clays Upon Different Oils

Since bleaching appears to be adsorption predominantly, and therefore relatively uncomplicated by other decolorizing reactions, the solution to one of its puzzling features becomes more readily explainable, the efficiency variations between clays upon different oils.

For example, if twice as much of one clay is required to bleach an oil as another clay, it would be expected the same relationship would hold for all oils. Unfortunately for the refiner and the clay manufacturer, such is not the case. The clay requiring double the dosage on the first oil may be equal to the other clay on a second oil, and takes four times as much on a third oil, etc.

It was believed that the total adsorptive capacity of clays on different types of oil might help explain the variation since the ordinary color reduction in a bleach represents only a fraction of the capacity. Some tests were made to this end.

The adsorptive capacity of natural vs. activated clay provides an ideal comparison of this kind because of the wide range in their physical characteristics and respective capabilities of bleaching different types of oil. As an example, natural clay has a low active surface area and void space as reflected by a high apparent bulk density. Activated clay is the reverse, high surface area and void space, etc.

Natural clay is practically equal to activated in bleaching efficiency on many light colored, high quality oils, such as certain grades of cottonseed oil and coconut oil, lard and edible tallow. On the other hand, the clay is quite ineffective on dark oils, such as palm, sesame, inedible tallow and many grades of castor oil. In certain cases, a normal bleached color is impossible to attain without the use of a prohibitive dosage. For this reason, only activated clay is used in the industry on this type of oil.

TABLE III

Filtration Rate of Various Particle Size Fractions, Soybean Oil

Particle size fraction	Clay, %	Filtration rate, sec.
Very fine, dust	5	1,911
Medium, intermediate cut	5	309[a]
Coarse, tailings	5	159

[a] Normal for Bleaching Clay.

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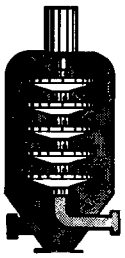

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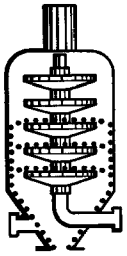

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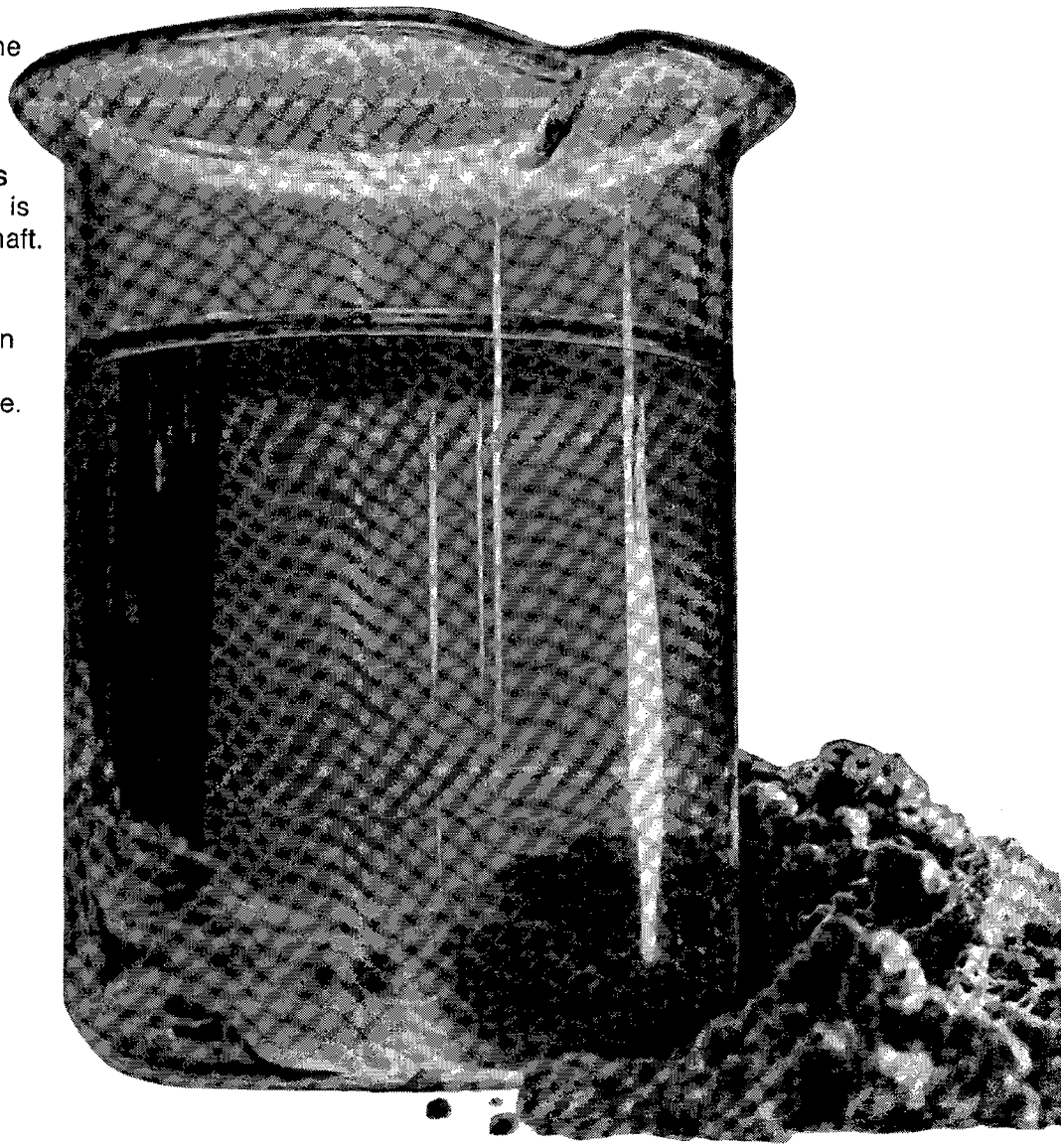

TABLE IV
Filtration Rate vs. Dosage

Clay, %	Filtration rate, sec.			
	Natural clay	Medium activated clay	High activated clay 1	High activated clay 2
2½	258	256	290	418
5	341	372	422	700
10	603	581	699	1,320

Total adsorptive capacity was determined, first by bleaching the oil under the AOCS open cup bleach conditions, filtering in a Buchner funnel, and reading the color. Fresh oil then was bleached with the filter cake, and this was repeated until the bleached color became constant. Adsorptive capacity per per cent clay was taken as the sum of the color reductions in the bleaches divided by the dosage.

In each bleach, the color reduction was taken as the difference between a blank (conducted under the same conditions except that no clay was used) and the bleached or residual color. This was employed to allow for any possible fading of the oil's color by heat alone.

Table II illustrates results on a normal quality soybean oil with 1% dosage, and a dark colored palm oil with 3% dosage, respectively, indicated a much lower adsorptive capacity for natural clay on the palm oil, relative to activated clay, than on the soybean oil. Actual capacities of each clay were much greater on the palm oil.

When the amount of color removal was extensive, as on the palm oil, the natural clay had a low capacity vs. activated. Evidently the low surface area of the former is a limiting factor, and thus it is unable to handle the color load. On the other hand, when the amount of color removal was small, as on the soybean oil, the capacity of the natural clay is much closer to that of the activated, and the low surface area was less of a factor.

Thus, the variation between clays in efficiency on different oils depends upon the two factors that determine their adsorptive capacity on these oils, viz., the clays' respective surface areas, and the amount of color and organic impurities to be removed. Other factors have an effect, such as pH of the clay, but are of less importance.

Also of interest in these tests was the percentage of total adsorptive capacity remaining in the clay after the initial bleach.

The amount remaining in the clay was fairly close on soybean oil, 40% for natural, 34% for activated, but on palm oil there was a marked difference, 34% vs. 73%, respectively. Not only did an equal dosage of activated clay to natural bleach the palm oil to a lower color, but a much smaller per centage of its capacity was used up in so doing.

Filtration Factors

Basically, the filtration rate in bleaching is inverse to the fineness of the clay's particle size. This is readily evident from a comparison of the laboratory filter rates of the particle size fractions, or cuts, segregated from an activated clay during milling (very fine, medium and coarse). Table III illustrates the relationship.

Filtration rate is inverse to the clay dosage. The more clay used, the thicker the filter cake, therefore the greater the resistance to flow. Table 4 shows the decrease in filter rate with increasing dosage on refined soybean oil.

Thus, of two clays filtering an oil equally fast when the same dosage is used, the clay with greater bleaching efficiency will filter a batch of oil faster since less clay is used to bleach to a given color. In the above, assume 2½% of medium activated clay and 5% natural clay are the dosages, in line with their efficiencies on soybean oil.

TABLE V
Filtration Rate vs. Unbleached Oil Color and Clarity

Oil	Oil type	Clay, %	Filtration rate, sec.
Refined soybean	Light color, clear	5	372
Refined palm	Dark color, clear	5	428
Inedible tallow	Dark color, turbid	5	585

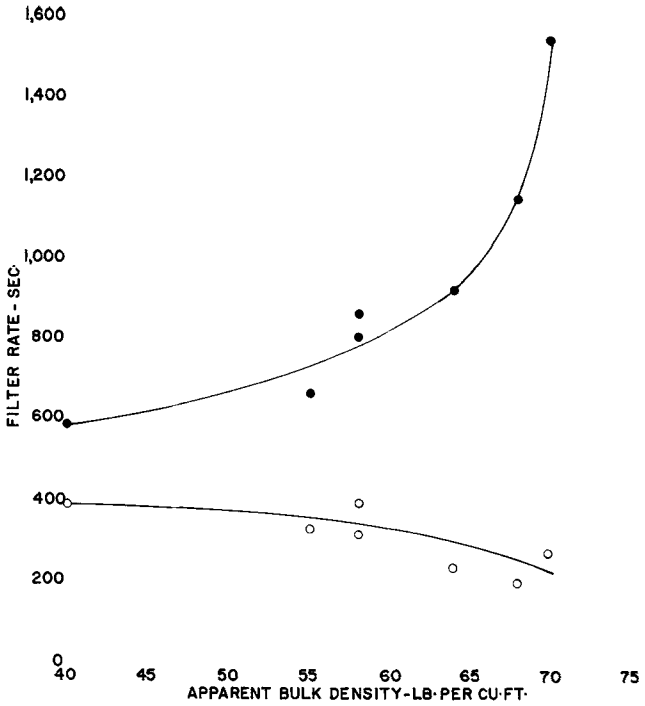

FIG. 1. Filter rate vs. apparent bulk density of clay on oils low and high in organic impurities. Refined soybean oil, low in organic impurities, ○; under-refined soybean oil, high in organic impurities, ●.

The filter rates would be: (a) medium activated clay, 256 sec.; (b) natural clay, 341 sec.

If 5% dosage were used for both clay, the medium activated clay would be slower, 372 vs. 341 sec. Filtration rate is inverse to the apparent bulk density of the clay when oils containing a high percentage of organic impurities are bleached, e.g., inedible tallow or an under-refined vegetable oil. For example, assume a natural clay filters a clear, light-colored oil as fast as an activated clay. The natural clay will filter an oil with a high per centage of organic impurities at a slower rate than the activated clay because its limited void space (reflected by a high bulk density) becomes more readily clogged with adsorbed impurities. Figure 1 illustrates the effect.

On a given clay, filtration rate is inverse to the amount of color and organic impurities in the unbleached oil. For instance, when a dark oil is bleached to normal color, more color is adsorbed than in the case of a lighter colored oil bleached to the same color level. There is more resistance to the oil flow due to more clogging of the clay's void space, hence filtration is slower. The same applies to bleaching an oil containing substantial organic impurities, except that the clay's intersticies become clogged both with impurities and color.

Table V illustrates the effect when different oils are bleached with an activated clay.

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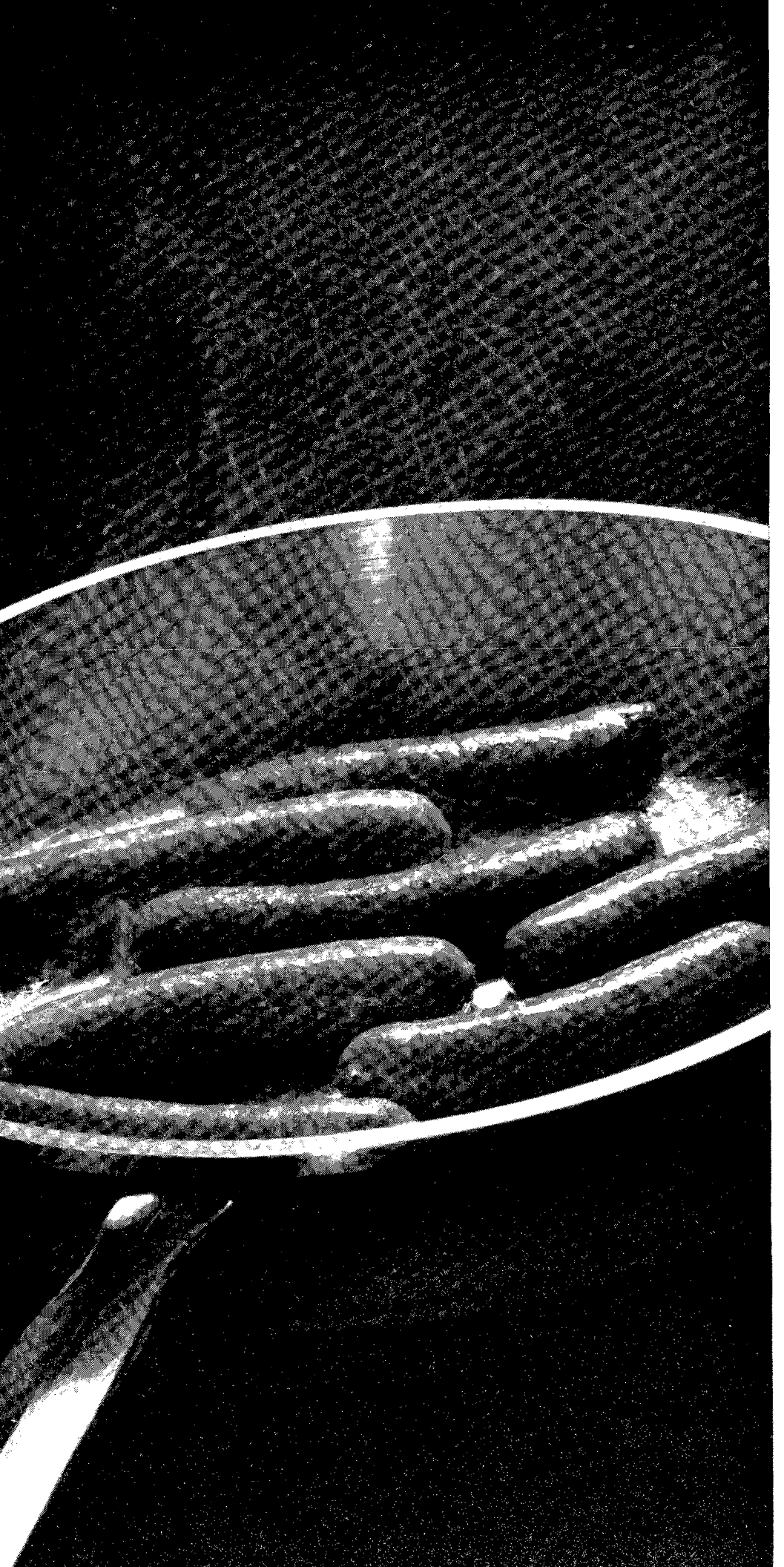

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