film. In varnishes both esters show properties closely akin to tung oil and, in fact, seem to have greater durability than tung oil varnishes upon exterior exposure. Perhaps at a later date we will be able to report in greater detail.

To summarize: optimum conditions for reaction of a fatty acid with a polyhydric alcohol to form an ester have been outlined; the value of catalysts has been found to be insignificant under these conditions. Some esters have been prepared and their properties discussed. From the qualities shown by these esters in varnishes it is felt that several of them are of value for the production of protective coatings. Blends of fatty acids to give certain definite properties to these synthetic esters will increase their value.

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Influence of pH of the Adsorbent on the Properties of Edible Oils and Fats

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IN THIS paper the phrase "pH of the adsorbent" refers to the pH of the water extract. Consequently, the numerical value depends on the conditions under which the extraction is conducted. In this work 1 gm. of adsorbent was stirred into 100 ml. distilled water, the mixture heated to 100°C., then cooled to room temperature, and the pH of the slurry determined electrometrically.

The pH of fuller's earth ranges from 7.0 to 10.0, depending on the source and the processing. Many active clays have a much lower pH ranging from 3.0 to 5.0, although a few are as high as 7.0. These activated clays are produced by the action of strong acids (HCl or H_2SO_4) on certain natural clays. The function of the acid is complex (1), some of it existing as an adsorbed layer or film.

The pH of a carbon may arise from various causes. Surface oxides (2) may be present, also, there is partial evidence that traces of some organic acids are formed during certain activation processes. Generally, however, the predominating factor is the effect of mineral constituents, some of which are derived from the original carbonaceous material whereas others are purposely added before activation to catalyze the development of certain adsorptive powers. Many of the mineral constituents undergo chemical change during the activation stage. In most processes the end products are alkaline resulting in the carbon exhibiting a pH from 8.0 to 11.0. However, in some processes the mineral constituents have final pH values as low as 3.0.

For some purposes the carbons are marketed without further processing but in many cases the pH is adjusted to a more neutral range by adding acid or alkali according to which may be required. In other cases the carbon is washed and in still others a combination of these treatments is employed.

When the adsorption of color is conducted from an aqueous solution the pH can have several effects, one of which is an indicator change. If we acidify an alkaline phenolphthalein solution, the pink color disappears. Similarly, if we add sufficient adsorbent of a low pH to an alkaline phenolphthalein solution the color will disappear from the filtrate but here we cannot know whether this is an indicator change or adsorption unless we apply a further test, e.g., add alkali to bring the filtrate back to the original pH.

Apart from any indicator influence, the pH of an adsorbent can have a marked influence on adsorption from aqueous solutions, especially when used in dosages sufficient to alter the pH of the solution. The degree of ionization or the chemical form of certain constituents may be altered so as to change the adsorbability, e.g., oxalic acid is strongly adsorbed by many carbons, whereas the adsorption of sodium oxalate is practically nil. Moreover, the solubility of many adsorbable substances is affected by pH conditions. Since the extent of an adsorption is a net effect of the relative attraction of the adsorbent as compared to the pull of the solvent, a change of solubility alters the extent of the adsorption.

THE influence of the pH of the adsorbent is not limited to aqueous solutions — for it has been found to affect adsorption from other solvents—sometimes with seeming inconsistencies. Thus, in adsorbing the dye, Ponceau 3R, a low pH carbon gave greater apparent adsorption from alcohol, whereas a high pH carbon was more effective for adsorbing this dye from pyridine. In contrast, a solution of Congo Red in pyridine was more effectively decolorized by a low pH carbon. These irregularities are only partially due to differences in adsorbability since color changes are also involved. The inconsistencies just quoted are purposely selected to show the complex factors that can exist.

However, reasonable consistency is found in very many cases—and this is true of the application of adsorbents to fats, oils, and waxes (3). There is rather consistent evidence that a high pH (above 9.5) is detrimental to color removal and sometimes this is true of pH values below 4. The reason for the detrimental influence of a high pH of an adsorbent is not clear but has been attributed to a catalytic action of certain alkaline chemicals in promoting oxidation. When the pH is low (particularly when

TABLE 1.

Three samples of Beeswax treated with 3% carbon. The carbon was adjusted to different pH values as shown. Lovibond colors read in 2⅝ inch column. Color of original wax too dark to read.

pH Carbon	Beeswax Sample 1		Beeswax Sample 2		Beeswax Sample 3	
	Yellow	Red	Yellow	Red	Yellow	Red
11	....	....	....	....	50	10.0
10	35	4.4	....	....	....	....
9	....	....	....	....	35	6.5
8	....	....	35	4.6	....	....
7	20	2.7	....	....	35	6.0
5	....	....	35	3.6	35	5.5

sulfuric acid is used for pH adjustment) the film of acid on the surface of the adsorbent may react chemically with the oil and produce a darkening effect such as occurs when concentrated sulfuric acid is added to an oil.

Table 1 shows the decolorization of three different samples of beeswax, using 3% of active carbon. The same brand of carbon was adjusted to different pH values from 5 to 11, and within this range a lower pH value generally gave better decolorization. Similar behavior was noted in case of Menhaden Oil (Table 2) and Peanut Oil (Table 3).

TABLE 2.

Decolorization of Menhaden Oil, using 3% Active Carbon adjusted to different pH values.

pH Active Carbon	Yellow	Red
9.0	35	3.8
5.0	35	3.2
Original Oil	35	7.0

TABLE 3.

Decolorization of Peanut Oil, using ¾% Active Carbon adjusted to different pH values. The original oil was 35 Yellow, 3.4 Red, 0.08% F. F. A.

pH Active Carbon	Yellow	Red	F. F. A.
9.5	20	2.2	0.08
8.5	20	1.8	0.08
5.0	20	1.5	0.08
Original Oil	35	3.4	0.08

Table 4 shows the effect of the adsorbent pH on a sample of Coconut Oil. The effect on color removal is not great but there is a definite trend toward better decolorization at the lower pH values of the carbon.

TABLE 4.

Decolorization of Coconut Oil, using ¼% Active Carbon adjusted to different pH values.

pH Active Carbon	Yellow	Red	Odor
8.6	20	2.2	Very good
7.0	20	2.2	Very good
6.1	20	2.1	Very good
4.5	20	2.1	Good
3.8	20	2.0	Slightly off
2.7	20	1.9	Bad
Original Oil	35	5.2	Good

Table 5 covers a similar treatment of Cottonseed Oil. Here an optimum range is observed since pH (6.1 to 4.5) gave better decolorization than did higher or lower values.

Table 6 shows the decolorization of Cottonseed Oil by different brands of commercial active clays having different pH values. Better results generally obtained at low pH values, but it is to be recognized that other properties may be involved since the clays were from different sources and may differ in other properties. This latter point was provided for in a subsequent experiment by adjusting one brand of clay to different pH values. The results (Table 7) show that lowering the pH to 4.0 was beneficial, but a very low pH of 2.5 caused increased color.

TABLE 5.

Treatment of refined Cottonseed Oil, using 1% Active Carbon adjusted to different pH values.

pH Active Carbon	Yellow	Red	F. F. A.	Odor	Kreis Test
8.6	35	5.2	0.040	Excellent	Slight
7.0	35	4.7	0.040	Excellent	Slight
6.1	35	4.5	0.040	Excellent	Slight
4.5	35	4.5	0.044	Good	Positive
3.8	35	4.8	0.046	Slightly off	Positive
2.7	35	5.2	0.052	Bad	Positive
Original Oil	35	7.2	0.044	Good	Positive

TABLE 6.

Decolorization of Cottonseed Oil, using ¾% Active Clays. These were different commercial brands of clay.

Clay Used	pH Clay	Yellow	Red
A	7.5	35	3.6
B	5.4	35	2.8
C	4.0	35	2.6
D	4.0	35	3.0

Tables 4 and 5 reveal that carbons with a pH of 4.5 or higher had a beneficial effect on odor but when the pH was reduced to 3.8 and 2.7 an increasingly detrimental effect on odor was observed. Such increased odor at low pH values was not due to a failure of the carbon to remove any of the original odor but resulted from the development of a foreign odor. Our data is inadequate to explain the exact mechanism of the reaction producing this odor, possibly the acid film on the adsorbent reacts chemically with the oil, a point which is indicated by the increase in apparent Free Fatty Acids shown in Table 5. It is to be noted that although only ¼% of active carbon was used on the Coconut Oil, and 1% on the Cottonseed Oil, yet both oils show the same parallel relation of odor development to the pH of the carbon.

TABLE 7.

Decolorization of Cottonseed Oil, using ¾% of same clay, adjusted to different pH values.

pH Clay	Yellow	Red
9.3	35	4.9
5.4	35	2.8
4.0	35	2.6
2.5	50	15.0
Original Oil.	35	6.6

CLAYS are much less effective than carbon for odor removal. We have no data on the influence of pH of clay on odor development, although from general experience it appears the pH of clay can be somewhat lower than that of a carbon before a foreign odor develops. However, this belief should be checked by a definite study.

Adsorbents frequently effect a slight reduction of F.F.A. and in this the pH has but little influence except where adsorbents with very low pH are employed. This is illustrated in Table 5 where the carbon with a pH value of 6.1 or higher gave a very slight reduction in the F.F.A. but lower pH's caused an increase in the apparent F.F.A., possibly due to the dissolving of the acid from the surface of the adsorbent. These conclusions apply to a dry oil. Where adsorption is conducted on a moist oil, an alkaline carbon gives appreciable reduction of F.F.A. and this is attributed to the presence of moisture promoting a reaction of the F.F.A. with the alkali (in a high pH carbon) to form soap, which is readily adsorbed by carbon.

Only one experiment was conducted on the influence of pH of the adsorbent on the Kreis test (4), and this indicates that carbons with a pH of 6.1 or higher have a beneficial effect on the Kreis test. This should be checked by further study.

Peroxide bodies present in an oil are adsorbed by active clays and carbons, and this work confirmed previous studies (5) that lowering the pH of an adsorbent results in increased removal of peroxide bodies. Although lowering the pH of an adsorbent produced an oil with a lower initial Peroxide Value, this is not necessarily reflected in greater stability. In fact, greater removal of initial peroxides is often associated with poorer stability—the Peroxide Value subsequently increasing at a more rapid rate. Whether this change is due to greater removal of stabilizing substances by adsorbents with a low pH or whether it is due to a chemical reaction occurring in the oil when in contact with low pH adsorbents is something we do not yet know.

The author wishes to express appreciation to Messrs. R. A. Hagberg, A. A. Aikey, and H. F. Laughlin of this laboratory for their cooperation in this work.

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Report of Soap Analysis Committee, AOCS; ASTM Committee D-12, 1944

DURING the current year the Soap Analysis Committee has been engaged in cooperative studies on two projects as follows:

1. Methods of analysis of special soaps containing synthetic detergents.
2. Two proposed methods for the determination of free caustic alkali and carbonate in potash paste soaps.

Notwithstanding the urgency of other matters and the shortage of manpower in most laboratories, we are pleased to report that 15 laboratories were able to cooperate in the program.

1. Methods of Analysis of Special Soaps Containing Synthetic Detergents

It should be explained that this study was initiated because of the large quantities of these soaps now being produced for the Army and Navy departments. Briefly, these products, in bar form, consist of homogeneous blends of one or more of the various synthetic detergents (usually sulfated types) with soap. Moisture contents of most of the brands being produced will fall in the range of 5 to 30%, active synthetic contents from 10 to 25%, anhydrous soap contents from 25 to 40%, the balance being largely inorganic salts including sodium sulfate, sodium chloride, sodium silicates and sodium carbonates. A small amount of unsaponifiable matter is sometimes present due to so-called unreacted oily material present in some of the synthetic detergents in common use.

At first glance it would appear that the analysis of such products would be readily approached on the same analytical basis as that of the ordinary soaps, but the presence of the active components of the synthetic detergents and the appreciable amounts of inorganic salts has made it necessary to modify the usual procedures considerably. Consequently, the committee is of the opinion that it is desirable to publish a rather complete set of modified analytical methods to cover these special types of soap.

The methods employed in these studies were based on the Army and Navy procedures included in the specifications for these types of soaps, incorporating such modifications suggested by the experience of the various cooperating laboratories as appeared to be advisable. Three samples of these special soaps, selected from commercial production of three companies manufacturing these products, were used in these studies by the 15 collaborating laboratories. The results of the collaborators on these three samples are shown in Tables I, II, and III. Considering that most laboratories participating in this work did not have much experience with some of these methods, it is considered that the results, for the most part, are in good agreement.

A meeting of the main committee was held in Chicago on October 24, 1944, for the purpose of reviewing and discussing the results of the cooperative work. It was the consensus that the data indicated, with some further slight modifications of the methods, a satisfactory analysis of these types of detergents can be obtained. Below is a summary of the action taken by the committee on the individual determinations.

Moisture. Two methods were used in the studies, the standard oven moisture at 105°C. and the standard distillation method. The committee voted to offer the oven method as the tentative standard because it gave more consistent results than those obtained by the distillation procedure. In the oven method the average deviation from the mean was 0.45% as against 0.89% for the distillation method.

Free Alkali or Free Acid. The standard procedure for ordinary soaps was used. Although the percentages shown in the tables are about equally divided, both acid and alkaline, the results are all considered