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FULLER'S EARTH OF LOCAL ORIGIN AND ITS APPLICATION TO BLEACHING OF VEGETABLE OILS

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Dedicated to my Parents

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Part A.

Introduction

ABSTRACT

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Fuller's Earth of Local Origin and Its Application to Bleaching of Vegetable Oils

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In summarizing the thesis, we may say that the clay commonly called "keel" obtainable from Azaz near Aleppo has good bleaching properties and can be used for bleaching oils and waxes. This local fuller's earth is comparable with the good English Earths. The English fuller's earth removed 80.4 % of the color in a sample of cottonseed oil, while the local earth removed 76.9 %.

Chemically the local clay is high in silica content and according to King, is of the unactivable kind. It is of an average density, high in volatile matter and is neutral. Its values of the constants of Freundlich's isotherm are,

$$k = 0.3 \quad \text{and} \quad n = 1.35$$

These being true when the earth is used in low concentrations. The above values mean that the earth is most efficiently used in successive stages, the concentration in each stage not exceeding 5 % of the weight of the oil.

The local fuller's earth shows increase in efficiency with increase of mesh size down to 180 and even lower. It is not worth activating the earth, as the increase in the efficiency is negligible, but the best treatment is to heat the raw earth up to 200 deg. C. for two hours.

INTRODUCTION

The immediate purpose of undertaking this whole work was to investigate the possibility of obtaining fuller's earth of local origin. Up to the present time all fuller's earth used in this country has been imported mostly from England, the U. S., Italy and France. A table showing the imports and their values for different years is given below. The table is not restricted to fuller's earth only, but also includes pumice stone and diatomaceous earth used in filtration. In French, tarrif number 181 B of the customs reads (1) : "pierre ponce, tripoli, et matieres minerales similaires pour aiguiser, polir et nettoyer."

Year	Imports	Value
1947	25,140 kgs	13,258 LL.
1948	15,515	18,942
1949	7,962	5,994

The vegetable oil industry which uses most of the fuller's earth imported is a major industry in Lebanon and is still a growing one. Statistics (2) show that in 1949 there were 18 vegetable oil factories with a capital investment of 5,414,000 pounds. Their production other than olive oil was 3,200 tons of oil. The consumption in Lebanon was 4,000 to 5,000 tons, excluding olive oil. Since that time at least four new factories have been built.

Before starting work, we wanted to learn as much as possible about fuller's earth clays in Lebanon. Mr. Dubertret* was interviewed. According to him no work had been done on this subject.

As the thesis will show in later sections, a fuller's earth supply was found to have good bleaching power, in the raw state, comparable with an activated English sample of good quality. The local earth was then processed in an effort to improve its quality.

(*) Geologist to the Lebanese Government.

Part B.

Theoretical Discussion

Section I

FULLER'S EARTH -- GENERAL CONSIDERATIONS

Fuller's earth has long been known as a variety of clay-like materials which have a common property of adsorbing grease and oil. The earth has long been used as an adsorbent. The Chinese have used the earth for decolorizing vegetable oils for over a thousand years. The earth was used for centuries in England, for the deoiling and degreasing of textiles, a process termed "fulling", hence the name fuller's earth. It was, however, only in 1855 that the first British patent was obtained for the p urification of oils by the treatment with clays(3).

1. Structure and Composition

Minerologically, the fuller's earth group is not a sharply defined group. It is distinguished from the bentonites by its high adsorptive power, as most of the bentonites have little natural adsorptive power(4). Materials of the fuller's earth group are mixtures and some approximate kaolinite ($Al_2O_3.2SiO_2.2H_2O$) in composition. Optical and x-ray data indicate that montmorillonite is an important constituent. Johnston (4) says that montmorillonite and attapulgite together compose more than 90 % of the mineral constituents of the earth. Other major constituens are quartz, muscovite, glauconite, amorphous silica, microcline, orthoclase, ablite, amphibole and biotite (4).

2. Chemical Analysis

There is no relation between the chemical analysis and adsorptive power(7)

In the following analyses clays A and B are good bleaching agents, but are quite different in composition while the earths B and C are very similar in composition, but C has no bleaching action. A high silica to alumina ratio appears to be a characteristic of earths having good bleaching properties (6). However, the efficiency of the earth must be determined by actual tests as the chemical analysis is of little value in showing bleaching power.

Constituent	A	B	C	D	E	F	G	H
SiO_2	72.95	58.10	58.72	47.00	67.78	53.3	62.6	63.2
Al_2O_3	12.65	15.43	16.01	23.30	12.75	13.3	20.1	14.5
Fe_2O_3	4.03	5.25	2.12	6.95	4.31	9.8	6.0	2.2
MgO	0.57	2.44	3.30	trace	11.60	2.0	2.0	2.3
CaO	1.00	1.75	1.05	2.90	1.63	4.9	2.0	1.5
Na_2O	0.20	0.27	2.11	5.95	0.12	1.8	---	0.4
K_2O	0.68	0.66	1.50		0.76		---	

(A) From Florida ref. (5)
(B) and (C) ibid.
(D) Fuller's earth from Rajputana, India, Bohla ref. (8)
(E) Georgia Florida fuller's earth, Johnston ref. (4)
(F), (G) and (H) are fuller's earth from England, Germany and Japan respectively, King ref. (3)

3. Effect of Organic Ingredients

Organic ingredients have little or no effect on the activity of the earth. Eckart (10) extracted the organic matter from five-gram samples of several earths with water, acidified the extract, and titrated it with potassium permanganate. The amounts consumed were equivalent to only 0.00064 to 0.00136 g. of humic acid. The gravimetric determination of organic matter when attempted was complicated by the difficulty of removing water.

4. Density

Bulk density usually falls between 28 to 70 lbs./cu.ft. Lower bulk densities are correlated with higher adsorptive power, finer state of division and low water content (4). Lanthrop gives the variations in specific gravity as 1.75 to 2.50 g./cc.

5. Acidity

Fuller's earth is usually neutral as to acidity. It may, however, be slightly acid, the mean of neutralization being 1.5 % of CaO (11). Earths having high apparent acidity have stronger bleaching effect than those more nearly neutral, hence their use for low grade inedible, darkly colored oils in which the acidity of the earth used is relatively unobjectionable.

6. Uses

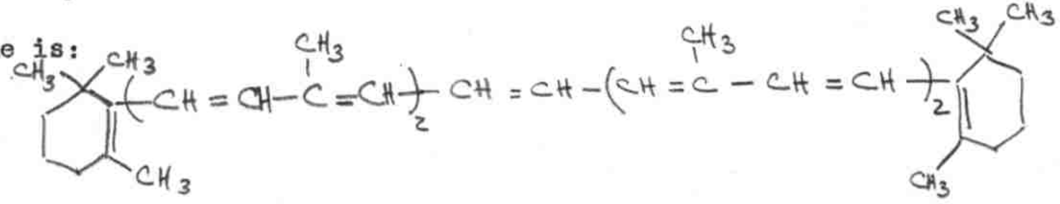
Other than its use as an adsorbent for animal, vegetable and mineral oils, fats and waxes, fuller's earth is used as a catalyst, as a neutralizer for bases, as a promoter for alcohol fermentation, and as a filler and ingredient in cements and the like (3,4,6,12,13,14).

Section II - COLOR OF OILS

Since a principal use of fuller's earth is as a decolorant for vegetable fatty oils, the nature of the coloring matter in the oils is important in this study. Other than the carotenoid pigments, that are responsible for most of the characteristic yellow and red colors in fatty oils, there occur in such oils varying amounts of other pigments such as gossypol, chlorophyll and resin pigments. These pigmentary materials will be discussed separately in the order of their importance.

A. Carotenoid Pigments

This class is made up of carotenes and xanthophylls. Carotenoid pigments in cottonseed oil was found by Palmer and Eckles in 1914, with the help of chromatographic adsorption characteristics and of adsorption spectra, to consist of equal parts of carotene and a total of five xanthophylls (15). Structurally they are highly unsaturated hydrocarbon chains of isoprene units. The structure of β-carotene is:



Factors which will reduce the color due to carotenoid pigments are as follows:

1. Saturation of the Molecule. The colorless or nearly white condition of hydrogenated fats is evidence of the effect of saturation (12).

2. Heat Treatment. The molecule is unstable to heat (12). Bleaching is partly effected therefore, by high temperature treatment, as in steam deodorization.

3. Oxidation. The color may be destroyed by oxidation (12), but oxidation is impractical because it develops rancidity in oils before bleaching them.

4. Refining. Color due to carotenoid pigments may be lightened by alkali refining (12), although probably the decolorization is physical rather than chemical, the pigments being adsorbed on the soap formed by the alkali.

5. Fuller's earth. The carotenoids are readily adsorbed by fuller's earth or activated carbon. Any oil having carotenoid pigments only may, therefore, be bleached to any desirable degree if adequately treated (12). As to the extent of the concentration of the carotenoid pigment in oil, it is reported (12) that palm oil has 0.1 % α-and β-carotene, a higher concentration than in any other oil.

B. Gossypol Type Pigments

Gossypol is a toxic phenolic substance present in raw cottonseed to an appreciable extent and in other oil seeds to a lesser extent (12). The higher the oil content of cottonseeds, the higher is the proportion of gossypol (16).

Though the structure is not yet completely elucidated, Carruth (17) in 1918, considered that gossypol was a phenolic compound of the empirical formula

$$C_{30}H_{30}O_9 \quad \text{or} \quad C_{30}H_{28}O_9$$

Clark (18) in 1927 found the formula to be

$$C_{30}H_{30}O_8$$

Gossypol combines readily with sodium hydroxide and therefore is readily removed upon alkali refining of the oil (12). Royce and his co-workers (19) reported that the gossypol content of crude oils (hydraulic pressed) ranges from 0.039 % to 0.210 % and the average concentration to be about 0.05 %.

Other pigments related to gossypol and that occur in vegetable oils are gossypurpurium, gossycaerilin, and gossyfuloin (20).

C. Chlorophyll Pigment

Chlorophyll has been detected in the oils by means of its characteristic absorption band in the visible region. Normal soybean oil contains ca. 1500 μg chlorophyll per liter (12). Very little of the chlorophyll in crude oils is removable by alkali refining, but it appears to be completely removed by bleaching (20).

D. Brownish Pigments

Certain brownish colors in oils of inferior quality are due to such decomposition products of proteins and carbohydrates (12). Some of these coloring materials are exceedingly difficult to remove by ordinary processing methods.

E. Resin Pigments

Some investigators attribute part of the dark color of crude cottonseed oil and other oils, particularly drying oils, to the presence of resin pigments (20).

Section III - COLOR STANDARDS AND MEASUREMENT IN OILS

It still is the practice to measure the color of vegetable oils by the use of the Lovibond tintometer. This however is not adequate for quantitative work for the following reasons:

1. The most important objection lies in the fact that the Lovibond system of colors is not additive, hence it is not proportional to the coloring matter in the oil (21). Two solutions of the same strength having the same kind of coloring material, upon mixing, usually come to have a different color value from the average of the colors of the two solutions. Similarly a solution, upon dilution to half the concentration, may have a color value other than half the original.
2. The Lovibond system is unsuitable for the measurement of very dark colors. This objection applies more to mineral oils than to vegetable oils, since vegetable oils seldom are as dark as the mineral oils. Some vegetable oils, however, are sufficiently dark as to lead to difficulty.

In view of the above disadvantages, several methods of "true" color determinations have been devised.

A. Duboscq Method

Parsons and Wilson (21,22) developed a method by which the color of the oil is compared with that of a standard oil in a Duboscq colorimeter. The color of the standard oil is first determined by comparison with Lovibond color glasses. Color values of the unknown are expressed in terms of this primary standard, being inversly proportional to the depth of the oil required to match the intensity of color of the unknown with the standard. If Beer's law is followed, the color units are proportional to the concentration of the coloring matter in the oil. Tables have been constructed by these same workers, correlating Lovibond color and true color for mineral oils.

This Duboscq method was intended originally wholly for mineral oils. One disadvantage is that, when applied to vegetable oils, much difficulty is encountered in trying to match the colors of the standard and the unknown, because of the variation in the qualities of colors as well as in the intensities.

There is another difficulty (22) in using the Duboscq colorimeter with vegetable oils; at different ranges, the ratio of the color of standard to that of the unknown is not constant. Thus if a standard and a bleached oil match at 5 and 10 mms. respectively, at a deeper range they might match at 15 and 29 mms respectively, thus having a ratio of 2 in the first case and 1.93 in the second. This has been found the case when different kinds of oils are being compared.

B. Modified Lovibond Method

Bailey says that for most purpouses and in the case of most oils, the color of the fat or oil is satisfactorily expressed in terms of red Lovibond units (12). In matching the color of a sample of oil, it is only necessary, he says, to approximate the yellow color in order to obtain a satistactory match with the red glasses. In other words he found that the red component of the color of the oils is additive, though the yellow is not.

C. Spectrophotometric Method

Because of the above mentioned difficulties in the Lovibond and the Duboscq systems, refiners have resorted sometimes to spectrophotometric evaluation of oil colors for both research and plant work (12). In 1950 a spectrophotometric method for the determination of oil color was adopted as a tentative method by the American Oil Chemists' Society (23).

D. The F. A. C. Colors

Some inedible tallows and greases are too dark to be graded in terms of the Lovibond system, even with a thin cell. For the approximate evalu~~e~~ation of colors of such fats, the Fat Analysis Committee of the American Oil Chemists' Society has provided an arbitrary system of color standards consisting of sealed vials of solutions of vaious inorganic salts (24). The color of any fat sample may be determined by comparing with the various standards untill the nearest match is obtained.

Section IV - THEORIES OF ADSORPTION

As far back as 1785 charcoal was known to possess the property of removing coloring matter from solutions. The earliest systematic experiments were performed by T. de Saussure in 1814. He employed a number of porous materials as adsorbents (25).

We should clearly distinguish between adsorption and absorption. The former is a strictly surface phenomenon, pertaining to a higher concentration of a solute at a solid or liquid surface than in the bulk. Absorption, on the other hand, refers to a more or less uniform penetration. The surface of liquids and of solids is under strain and there exists a residual field of force. Therefore there will be a tendency for the free energy of any surface to decrease and it is this tendency which is responsible for adsorption (25).

Actually it is hard to distinguish between adsorption and absorption, especially when dealing with fuller's earth and oils, as chemical forces may also be involved other than physical surface phenomena, and the whole effect probably involves some features of both adsorption and absorption.

There are two approaches to this subject. 1. the surface of the adsorbent may be considered as acting by virtue of molecular attraction and of chemical forces, and 2. the adsorbent may be considered as providing an interface of large area, at which a solute capable of lowering the interfacial tension may accumulate. The first approach is adopted here because it is more suited for our purpouse and also because little information is available concerning tensions at solid-liquid interfaces (25).

According to this first explanation, adsorption is directly proportional to concentrations up to a limit. In experiments on the adsorption of acetic acid and of dyestuff from aqueous solutions by different adorbents, the amounts adsorbed increase with the concentration of the solution, reaching a maximum, beyond which concentration has no further effect on adsorption. Such results suggest the formation of unimolecular layers on the surface (25). Langmuir upon this assumption derived a relationship between concentration of solution and adsorption and as se shall see, this agrees to a large extent with experiments. However we cannot, on this basis alone, say that the adsorbed layer is one layer thick.

A. Freundlich's Isotherm

The variation of adsorption with concentration can be represented empirically by the equation of Freundlich (26), provided the temperature is kept constant. The equation applies both to the adsorption of gases or solutes from solution:

$$\frac{x}{m} = kc^n \qquad \text{equation 1}$$

where x is the amount adsorbed, m is the amount of adsorbent per unit weight of the oil, and c is the equilibrium concentration. k and n are constants to be determined experimentally for each temperature, solute and adsorbent. They should be independent of concentration. The value of n is usually less than unity, but greater than zero. If it is 1, then the Freundlich isotherm will be equivalent to the distribution law:

$$x/m = kc \qquad \text{and} \qquad x/c = km = k_1$$

Taking logarithms of equation 1, we have,

$$\log x/m = \log k + n \log c \qquad \text{equation 2}$$

Thus if we plot x/m against c on a log log scale, the slope is a straight line and is equal to n and log k equals to the value at the intercept when c is unity. We will come later to the interpretation of the significance of k and n.

B. Langmuir's Adsorption Isotherm

While Freundlich's equation is an empirical one, Langmuir developed an equation on theoretical bases (27). Langmuir's theory is based on the already mentioned view that surface molecules have residual energies and tend to adsorb particles from the gas or a solution, these making a layer only one molecule thick. Moreover the striking molecules or particles tend to adhere on the surface for some time before leaving the surface again.

The rate at which molecules are adsorbed according to the Langmuir theory, depends on three factors, namely,

1. The number of particles s striking unit area of the surface per second.
2. The fraction of the surface area which is not already covered (1-g) where g is the fraction covered.
3. The fraction f of the total number of particles striking the bare portion and adhering to it.

At equilibrium, the rate of adsorption is equal to the rate of desorption or evaporation, hence,

$$gr = fs(1-g) = fs - gfs \qquad \text{equation 3}$$

where r is the rate of evaporation from a completely covered surface.

$$g = \frac{fs}{r+fs} \qquad \text{equation 4}$$

Substituting K for the constant f/r, we have,

$$g = \frac{Ks}{1+Ks} \qquad \text{equation 5}$$

The fraction g is proportional to the amount of material x adsorbed by a definite mass m of the adsorbent. Also the number of particles s striking the surface per second is proportional to the concentration c of the solution at equilibrium. Equation 5 can be rewritten as

$$x/m = k\left(\frac{Kc}{1+Kc}\right) \qquad \text{equation 6}$$

This is known as Langmuir's adsorption isotherm.

At very low concentrations, or for poor adsorbents, the fraction g is small because a very small part of the surface is covered and (1-g) is nearly equal to unity, so that at equilibrium, we have,

$$gr = fs$$

and

$$x/m = Kkc$$

$$x/m = K_1c \qquad \text{equation 7}$$

Under these conditions, the amount of gas adsorbed is directly proportional to the concentration of the solute.

When on the other hand, adsorption is great and the adsorbent is of good quality, then almost all of the surface of the adsorbent is covered (at equilibrium), the fraction g is almost unity, so that equation 3 can be written thus,

$$r = (1-g)fs$$

$$g = 1-\left(\frac{r}{fs}\right)$$

so that

$$x/m = k\left(1-\frac{1}{Kc}\right)$$

and

$$x/m = k - \frac{K}{kc} \qquad \text{equation 8}$$

As the concentration c increases, K/kc becomes smaller so that the amount of material adsorbed approaches a limiting value

$$x/m = k \qquad \text{equation 9}$$

So that the Langmuir isotherm assumes the form of equation 7 at low concentrations and the form of equation 9 at high concentrations. At intermediate concentrations it will therefore, assume the form

$$x/m = kc^{n}$$

where n lies between zero and unity. This is essentially the same as Freundlich's adsorption isotherm, and is an approximate representation of the amount of adsorption.

C. The Practical Significance of the Constants in Freundlich's Isotherm

The constants in the Freundlich equation have a practical significance(12). k may be considered as a measure of the activity or bleaching power of the adsorbant, while n is an indication of the manner of adsorption. Thus if two clays bleach in the same characteristic way, but have different adsorbing capacities, i.e. if k differs while n is the same, then the relative amounts needed to produce the same degree of bleaching is inversly proportional to the values of k. Suppose we have the two clays

(a) $x/m = 0.5c^{0.5}$

and (b) $x/m = 1.0c^{0.5}$

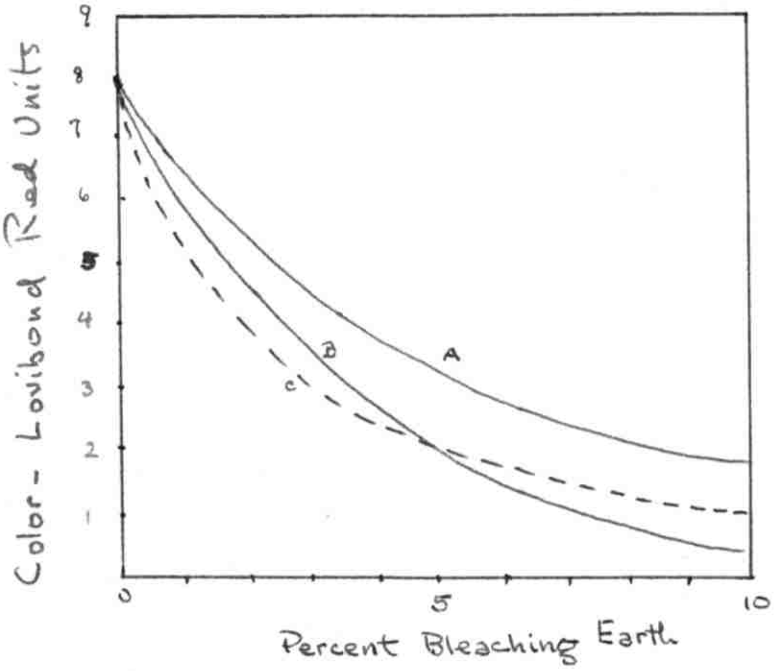
then to effect the same amount of bleaching, twice the amount of ~~bleaching, twice the amount of~~ (a) will be needed as of (b).

The value of n is important for determinging in what range an adsorbant is most effective (12). If n is high, the earth will be relatively effective in removing the first portions of color from the oil, but inefficient in effecting a high degree of decolorization. The reverse is true when n is low.

To illustrate the priciples involved, we reproduce a graph from Bailey (12) where the color (equilibrium) is plotted against the percentage of bleaching earth. These are calculated theoretically from Freundlich's equation. The original color is 8 Lovibond red units, so that $(x + c) = 8$, and

$$\frac{8 - c}{m} = kc^n$$

The values for m were calculated by assigning specific values for c, the color remaining at equilibrium.



Theoretical Bleaching Curve for Different Values of K and n

Earth (A)	k	0.5	Earth (B)	k	1.0	Earth (C)	k	0.6
	n	0.5		n	0.5		n	1.2

It is always desirable to have a large value of k, corresponding to a low position of the curve. A high value of n is also desirable, but not at the expense of k.

In comparing two adsorbants, it is imperative to specify the extent to which decolorization is desired. This it will be seen that if only 50 % of the color is to be revoved, earth (c) will be most efficient, even down to a color of 2.1 units, but beyond this, earth (b) will be more efficient.

In bleaching earths, the values of k and n vary widely depending on the earth, the oil and the method of bleaching. Bailey gives a table showing the values of k and n for twenty three cases of different bleaching agents, oils and conditions. The values of k range between 0.1 to 7.2 and the values of n range between 0.33 to 2.2.

It is evident from the Freundlich equation that for an earth that has reached equilibrium with respect to the adsorbant in a light oil, will still have adsorptive capacity for color in a darker oil, as the color removed is proportional to the original color, up to a limit. Hence the countercurrent principle of treating the oil, that is having fresh oil come in contact with used, nearly spent, earth and partly bleached oil coming in contact with fresh earth. In other words a small amount of adsorbed substance saturates the earth with respect to a partly bleached oil, but a greater ammount is needed to saturate the same amount of earth with respect to a fresh darkly colored sample.

It is also evident from the Freundlich equation, that the application of the adsorb~~a~~ent in successive small portions will produce greater decolorization than the same amount of adsorbant in a single dose. To illustrate this take the eath corresponding to

$$x/m = c$$

where k and n are both equal to unity. One gram in 100 g of oil will remove 50% of the color while if 5 g. of the earth were used all at once, they will remove 5/6 or 83.3 % of the original color, thus every gram removing about 16 % of the color. This it is not only necessary to use contercurrent bleaching in industrial operations, but to have a multiplicity of stages. With an infinite number of stages, the effect will be equivalent to that of continupus contercurrent flow. However Odeen and Slosson (28) reported that laboratory tests with acid activated clays in which multiple bleaching was less effective than the addition of the whole amount at once. Bailey (12) explains this on the basis that "prolonged heating and aeration to which the oil is subjected in such tests either converts the pigments to a difficultly adsorbable form, or develops new color through the production of new pigments or darkening of those previously present."

Section V - PREPARATION OF FULLER'S EARTH FOR USE AS DECOLORANT

Preliminary treatment of fuller's earth for use as a decolorant includes grinding the earth to the proper mesh, and heat treatment such as drying and ignition. Activation which may or may not be followed is discussed separately in a later section.

A. Grinding

Since bleaching with fuller's earth is to a large extent a physical phenomenon occuring on the surface of the particles, it follows naturally that the greater the exposed area of surface per unit weight of the earth, the greater the bleaching effect. Hence the necessity for grinding to the proper fineness. Putland (9) says that, since the coloring matter is retained in the pores of the earth, therefore the earth should be ground to a fineness that will expose a maximum number of those pores without rupturing them. This implies that in the case where bleaching power is plotted against mesh size, the curve increases to a maximum, then decreases, as we increase the mesh size. Putland says also that this maximum is at 150 mesh. Vollertsen (29) states that the bleaching power of fuller's earth increases with decrease of size of particle, at least up to 200 mesh, but that this increased fineness does not affect oil absorption.

According to Stourdze (30) the efficiency of fuller's earth increases with decrease of size of partiles but earths that are ground to too fine a mesh are of little value as they are very difficult to separate from the oil into which the objectionably fine particles have been mixed. This factor has to be taken into consideration especially when applying it to an industrial scale.

Another factor limiting the use of too fine earth, according to Phalen (31), is the flow of the oil when the oil is percolated through columns packed with the earth. The coarser the earth, the more rapid the flow, but the poorer is the bleach.

B. Heat Treatment

It seems to be commonly agreed (7,9,31,32,33,34,35,36) that heating up to a certain temperature, increases the activity of the earth, but heating beyond a certain point decreases the activity. "Fuller's earth has for its base a series of amorphous hydrous aluminum silicates that have a rather persistant colloidal structure" (35) that should not be destroyed.

Newman and Kober (36) say that "the single particles are viewed as gels low in water content and of various sizes. Heating up to 300-400 deg. causes no structural change, hence the increased activity must be due to freeing the particles of adsorbed water, thus making them capable for more adsorption."

Others say that part of the water of crystallization should be removed to obtain maximum efficiency (31,32) while others say that it is only moisture not molecularly held that is freed for maximum efficiency (7,9,33,35,37). A possible mechanism is explained in the next section.

Section VI - ACTIVATION OF FULLER'S EARTH

Around 1905-1906, it was discovered in Germany that clays which in the raw state are very poor adsorbents may by simple mineral acid treatment be changed to clays that are twice as active as ordinary fuller's earth. The activation of clays after that developed in many other countries so that activation now is very widely used. These clays are similar to fuller's earth, hydrated aluminum silicates. King(3) claims that acid activable clays have a relatively high alumina content as compared with ordinary fuller's earth. The ratio $SiO_2:Al_2O_3$ is 4-5 : 1 in case of ordinary fuller's earth, while for acid activable clays it is 2-3 : 1.

Activation is essentially the heating of the earth with a mineral acid of the proper concentration, filtering, drying, and then grinding the earth to the proper mesh.

The ways of activation are many. It is generally agreed that the acid used for the purpose should be dilute . British patent 176,355 recites a strength of 1 % of either hydrochloric or sulfuric acid. Nutting (39) also claims that the hydrochloric, sulfuric or organic acid used should be 1 % or less in concentration. Others claim, however, that the acid should be concentrated (40). Parekh and Vaidyer (41) made experiments with different earths at different acid concentrations and found out that optimum results are obtained at a concentration of 2 N.

Among the many acids proposed in the literature, sulfuric, hydrochloric, acetic, phosphoric and oxalic acids are the most important (3,39,40,42).

However, Parekh and Vaidya (41) found that hydrochloric acid was one half to one third as effective as sulfuric acid. It is even reported (3) that earth treated with hydrofluoric acid activates the earth by a simple etching process which increases the specific surface.

A typical change in composition of the earth due to acid activation is reported in Thorpe's Dictionary (3) taken from Eckart:

	Raw Earth	HCl Activated	Tartaric Acid Activated
SiO_2	59.98 %	73.64 %	63.31 %
Al_2O_3	19.84	13.46	17.85
Fe_2O_3	7.82	6.35	6.37
CaO	2.05	--	--
CO_2	1.61	--	--
Alkali	0.78	--	--
Valatile matter	7.92	6.63	8.41
	100.00	100.08	95.94

A description of a similar change is reported by Utescher (42).

The total amount of acid needed, calculated on the dry basis, varies between 25 % and 60 % to the total weight of the earth. Kauffman (43) says that 50 % by weight of the acid gave an increase in efficiency of 20 % to 40 %. Hungarian patent number 125,877 protects an invention where 52 % of acid is treated at 110 deg. C.

A too vigorous and intensive acid treatment is likely to decrease the activity of an activable clay (3). Activity is inhibited by alkali treatment (44) due to the precipitation on the surface of the particles aluminum and iron hydroxides.

MECHANISM OF ACTIVATION

Activation seems to be due not only to increased specific surface, but also to the replacement of metals such as Mg, Ca, Na, and K of the clay by H from the acid (3). Upon heating, the H and OH ions are driven off, open bonds are left (3,39) which select from the oil the darker and more basic constiturents

$$-\mathrm{Si(OH)}-\mathrm{O}-\mathrm{Si(OH)}-\mathrm{O}-\mathrm{Si(OH)}- \longrightarrow -\mathrm{Si(O-)}-\mathrm{O}-\mathrm{Si}-\mathrm{O}-\mathrm{Si(O-)}-$$

According to Nutting (39) it therefore appears that in naturally active fuller's earth the surfaces hold H and OH ions adsorbed in thin layers while in non active, but activable clays metals such as Fe, Al, and Ca already occupy the surface bonds. The former can be activated by heating, while the latter by acid treatment, and then heating. King (3) says in support of the above that the first constituents to be adsorbed in a mixture, are the unsaturated constituents. These are chamically retained on the surface and are not removed by solvents.

The same thing applies to heating after acid treatment of activable clays as to naturally occuring fuller's earth. A too low temperature is not sufficient and a too high temperature ruins the clay by dehydrating it.

Part C.

Experimental Work

Section VII

PROCURING OF MATERIALS

The original sample of clay to be examined for bleaching properties was obtained through Mr. Salah Hibri. Its origin was unknown to us. It was identified, however by some to be a clay from Azaz, northwest of Aleppo, there commonly called "keel". We asked a reliable friend in Aleppo to despatch us a sample of this "keel" obtainable from Azaz. The sample sent appeared to be identical with the one we had.

It is interesting to note that this "keel" is known to have a cleansing effect. It is used widely by the lower classes in Aleppo for body washing purpouses and especially cleaning (degreasing) the hair. It is powdered and made in the form of a thin paste and applied as such on the hair and body.

The samples of oil were also supplied by Mr. Salah Hibri. The first sample was crude unrefined cottonseed oil. It was alkali refined in the laboratory by treatment with strong (10 - 20 Bé, 7 - 15 %) solution of sodium hydroxide in slight excess (16,45). The whole was then heated to break the soap emulsion and the refined oil separated by filtration from the gelatinous soap and other associated impurities. The oil was then washed to remove excess sodium hydroxide and filtered again, a hot water funnel being used in the filtration to speed up filtration. The oil, now clean and free from fatty acids, phosphatids and other gummy and mucilaginous materials, was kept in a brown clean bottle and stored in a dark place.

The first sample of the unrefined oil was supplemented by a second sample. This sample, when obtained, was refined, but not bleached. It was filtered in the laboratory as there was some turbidity and inclusions which had to be removed. Filtration was hastened by adding the oil portionwise heated to about 100 deg. The refined oil was then kept in a brown bottle and stored in the dark.

In determining the bleaching power of the local earth, it was compared with an English fuller's earth of the best grade,

Activated Fuller's Earth Grade,
"Fulmont" 700 C

manufactured by

Fuller's Earth Union Ltd.
Redhill, Surry, England.

Section VIII - COLOR MEASUREMENTS

The color of the different oils was determined by the Duboscq colorimeter, as it has been shown that in this way the true addititve color of the oil can be determined by comparison with a standard of known color. The color of the standard unbleached oil was taken arbitrarily as 100 units, so that in every case the color of the bleached oil was compared with the original color, and calculated from the depth readings in the comparison cylinders by the formula:

$$\frac{\text{Color of unknown oil}}{\text{Color of original}} = \frac{\text{Depth of the standard}}{\text{Depth of the unknown}}$$

This method was originally intended for mineral oils, but in extending it to vegetable oils, difficulty was encountered in matching the colors, as the color is a composite of both yellow and red, that are adsorbed to different extents. To overcome this difficulty, ten readings were taken in each case and then averaged. The following are three samples of readings taken at different depths:

Example I Standard set at 5mms.
Readings 11.4, 11.2, 10.7, 10.3, 10.4, 10.8, 10.9, 11.0, 11.5, 10.5. mms.
Average 10.87
Maximum Deviation from average is 0.65 mm.

Example II Standard set at 5 mms.
Readings 27.3, 25.1 26.3, 26.5, 26.6, 26.3, 27.7, 26.8, 27.2, 27.1. mms.
Average 26.89
Maximum Deviation from average is 1.8 mms.

Example III Standard Set at 5 mms.
Readings 31.1, 29.0, 28.6, 31.3, 31.9, 30.3, 30.1, 31.2, 32.5, 30.6. mms.
Average 30.66 mms.
Maximum deviation from the average is 2.0mms.

It will be noted that the variation in readings increases as the color decreases. Ten readings were thought enough to give the average color.

To eliminate any errors due to inaccuracies in manufacturing the Duboscq colorimeter, or due to unequal distrubution of light, the standard was at all times placed in the left cup, and fixed at a depth of 5.0 mms.

Section IX

BLEACHING OF THE OIL

In bleaching the samples of oil, a modification of the official method of the American Oil Chemists' Society was used. The adaptation is as follows:

A. Description of Apparatus

1. Balance: Torsion balance sensitive to within 0.02 g.
2. Weights: Analytical
3. Refining cups: Pyrex beakers of 250 mls capacity, 6.5 cms. diameter and ca. 8.5 cms. height.
4. Stirrer: mechanical stirrer which w as adjusted to a speed of 250 ± 10 rpm with the help of a tacometer.

B. Procedure

1. Weigh 50 g. of the sample of oil into the refining beaker, add 6 % (3 g.) of the bleaching earth to be tested.
2. Commence stirring at 250 ± 10 rpm and heat immediately to 120 deg. C. requiring exactly five minutes.
3. Continue stirring for exactly five minutes. The temperature of the sample is kept above 105 deg. during this period.
4. Filter through a dry filter paper.
5. The color is determined by the Duboscq colorimeter, with the color of the standard taken arbitrarily as 100 units.

In the original official method (16) of the American Oil Chemists' society, 300 g. portions of oil are to be used for every determination. This was thought to consume too bulky an ammount for making quantitative bleaching tests.

The speed of stirring was not constant, due to fluctuations in the voltage resulting from heavy use of the electric current at times. It seems from the literature, however, that the speed of stirring has little effect (46, 47).

While heating the oil during the bleaching operation, it was found to be difficult to adjust the flame so that the temperature rises to 120 deg. in exactly 5 minutes. The variation in the time to reach 120 deg. was approximately ± 0.5 min.

Section X

LOCAL FULLER'S EARTH COMPARED WITH THE ENGLISH

The experiment was done on the refined cottonseed oil from the first batch. Bleaching and color measurements were effected as already described in sections VIII and IX.

Bleaching with the English earth

Standard: Unbleached cottonseed oil set at 5.0 mms.
Oil Compared: Bleached with English fuller's earth passing 180 **mesh.**
Readings: 23.9, 23.8, 24.1, 24.8, 26.2, 24.4, 26.3, 27.3, 25.8, 27.5.
Average: 25.42 mms.
Color of bleached oil: $\frac{5 \times 100}{25.42}$ 19.6 units

Color removed: 80.4 units

Bleaching with the Local earth

Standard: Unbleached cottonseed oil set at 5.0 mms
Oil Compared: bleached with local fuller's earth, without treatment, but passed through 180 mesh.
Readings: 21.3, 21.5, 19.7, 20.9, 23.2, 22.7, 21.8, 21.8, 22.8, 21.0.
Average: 21.67mms.
Color of bleached oil: $\frac{5 \times 100}{21.67}$ 23.1 units

Color removed: 76.9 units

It is seen that the English fuller's earth is slightly superior to the local earth. The oil bleached by it was 3.5 units lighter.

The local fuller's earth was also compared with activated charcoal grade:

Pittsburgh Activated Carbon
SG 8x30 mesh
EW-229-A

made by,

Pittsburg Coke and Chemical Co,
Pittsburg, Penn., U. S. A.

The carbon was ground and passed through 180 mesh so as to be comparable with the ground local fuller's earth in size of particle. The average reading was 33.1 mms, the standard being kept at 5.0 mms, so that the color came out to be 15.08 units.

Section XI - ANALYSIS

The moisture content, volatile matter, acidity and density were determined together with a complete quantitative analysis.

1. Moisture Content

Moisture Below 105 deg. 7.4435 g. were dried for 16 hrs. at 100-104 deg. C. The loss was 0.8642 g., so that the percentage loss was 11.61 %. Moisture Above 105 deg. 5.6041 g. were dried for 15 hrs. at a temperature of 115 - 125 deg. C. The loss was 0.6568g. so that the percentage loss was 11.72.

2. Volatile Matter

Volatile matter is determined as percentage loss in weight after a 10 minutes' ignition at 1000 deg. C. (6). The electric furnace we have in the laboratory reached only a maximum of 850 deg. The volatile matter was determined therefore on a 3.2501 g. sample heated at 810 - 820 deg. for 15 minutes. The loss was 0.7137 g. so that the volatile matter ammounted to 21.96 %.

3. Acidity

The acidity of a bleaching clay is the number of milligrams of potassium hydroxide required to neutralize the distilled water extract from 1 g. clay, with phenolphthalein as the indicator (6). A 4.8310 g. sample of earth was weighed in a 250 cc. volumetric flask, half filled with distilled water, and mechanically shaken for 45 minutes. The solution was left overnight, then made up to 250 ccs. One hundred cc$. were taken and titrated with 0.1 N sodium hydroxide. The volume needed was 0.2 cc. The acidity was then calculated and came out to be 0.580.

4. Density

The density is determined by dividing the weight of a sample, of earth by the volume occupied after five minutes of mechanical tamping and is calculated in lbs./cu. ft. (6). The earth was ground to pass 180 mesh, filled into a 50 cc. volumetric flask and weighed after five minutes of tamping. The weight was 37.215 g. earth, so that the density came out to be 0.7442 g./cc. or 0.7442 x 62.43 = 46.46 lbs./cu.ft.

5. Quantitative Analysis

In carrying the quantitative analysis, the procedure as outlined by Vogel (38) was followed. The sample was fused with sodium and potassium carbonate in a platinium crucible. The alkali metals were not determined but calculated by difference. In the carbon dioxide determination five trials were made before a difference of less than 0.5 % was obtained. The results are:

Trial	Carbon Dioxide
I	3.00 %
II	2.ol
III	2.57
IV	5.91
V	4.50
VI	4.32

The erratic results in cases I, II, and III we think were due to the poor adsorbent and the short adsorption tube. The adsorbent was sodalime, saturated with carbon dioxide, then displaced with pure air. One U-tube was used made up of two straight adsorption tubes joined with a tight fitting rubber tubing, with the glass ends of tubes touching. In trials IV, V and VI, an additional U-tube was used, and both were refilled with Ascarite (sodium hydroxide asbestos). The high value in IV is due to accidental opening of the valve in the calcium chloride tube between the reaction vessel and the absorption train. The following is a table of the complete quantitative analysis of the local fuller's earth:

SiO_2	51.57 %
Al_2O_3	10.31
Fe_2O_3 (total Fe)	7.65
MgO	5.17
CaO	.35
P_2O_5	absent
As_2O_3	absent
Loss on ignition	21.96
Total	97.01 %

Volatile matter comprises

CO_2	4.40 %
Moisture below 105°	11. 61
" above 105°	11.72

Alkali metals (calculated by difference) 2.99 %

The following table compares the density, acidity and volatile matter of the local fuller's earth with three other commercial materials (6).

	Local Earth	Florida-Georgia Type	Natural Bleaching Clay Southwest Type Fine Grade	Artificial Activated Clay Domestic Type Fine Grade
Volatile matter, %	21.96	16.0	16.0	21.0
Density lbs./cu.ft.	46.46	31.0	53.0	36.0
Acidity, mg KOH/g	0.58 neutral	neutral	neutral	3.5

Section XII

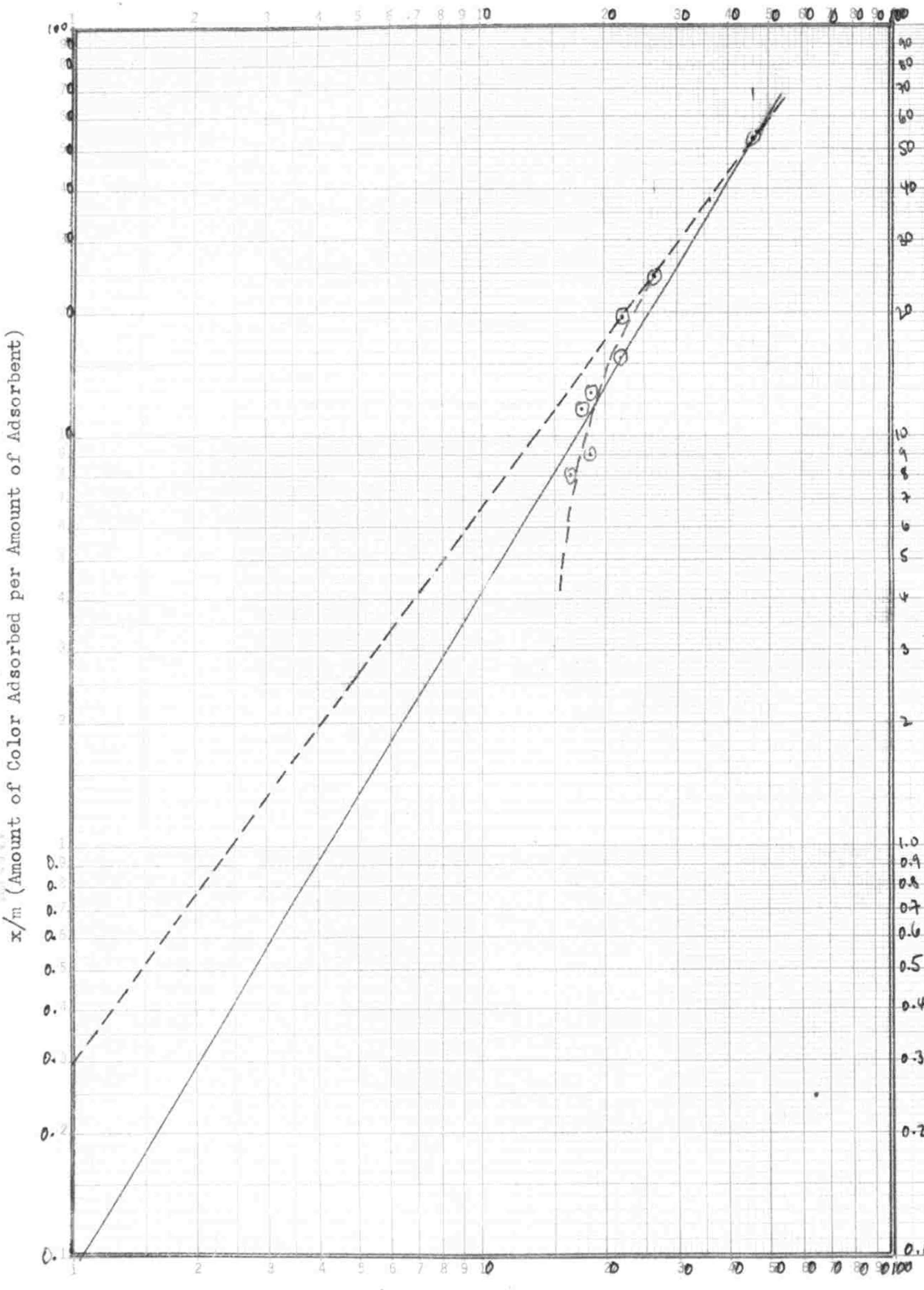
DETERMINATION OF CONSTANTS k AND n
IN FREUNDLICH'S ISOTHERM

In finding out the relationship between bleaching power and the concentration of the earth, ten 50-g. samples of the oil were bleached with local fuller's earth. The concentration of the earth ranged from 1 to 10.4 %. In all ten cases, bleaching was done as already described in section IX, except that the temperature to which the oil was heated was 124±2 deg. C. However in the cases where the percentage of the earth was 2 and 8 percent, the temperature accidentally reached up to above 130 deg. These will provide erroneous results if plotted in Freundlich's equation since this latter is valid at constant temperature. The following is a table showing the readings and values for c and x/m at the different concentrations:

Percent Earth	H in mms.	$C=(\frac{5 \times 100}{H})$	$X=(100 - C)$	x/m
1	10.87	46.08 units	53.92 units	53.92
3	18.89	26.45	73.55	24.52
4	22.56	22.17	77.83	19.46
5	22.68	22.03	77.97	15.59
6.3	26.89	18.59	81.41	12.92
7	28.39	17.61	82.39	11.77
9	27.45	18.22	81.78	9.09
10.4	30.66	16.31	83.69	8.05

Where H is the height in mms of the unknown oil as compared with the height of the standard in the Duboscq colorimeter. The standard

ADSORPTION ISOTHERM -- Refined Cottonseed Oil



was always kept at 5.0 mms. C is the color of the bleached oil, that of the standard being taken as 100 units. X is the units of color removed, and x/m is a measure of the bleaching effect.

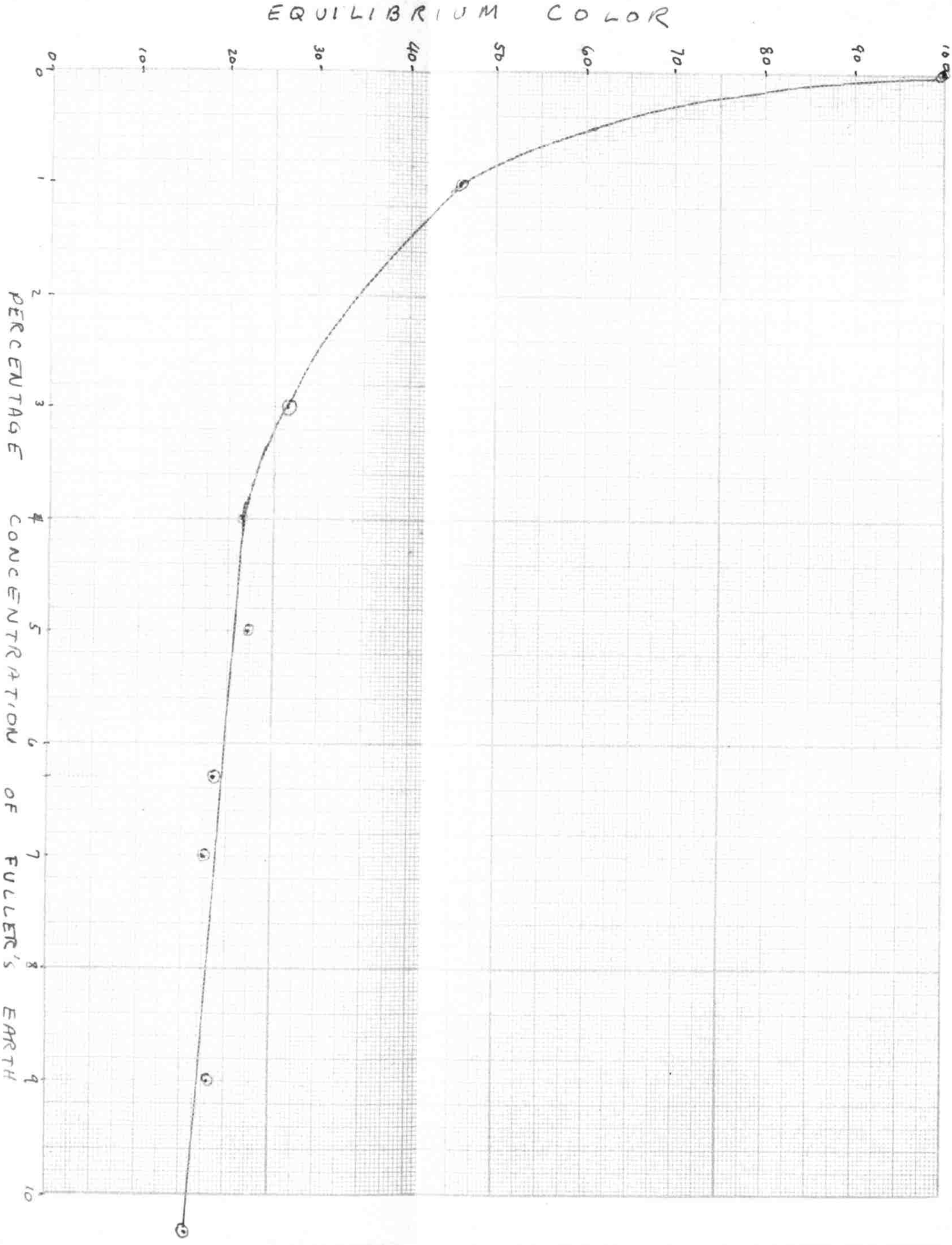
The graph on the opposite page was made by plotting on a log log scale the values of C against those of x/m. The best straight line was passed through the points and its slope determined. This gave a value of 1.68 for n. The value of k is the value of the intercept of the line with the x/m ordinate. This came out to be 0.1.

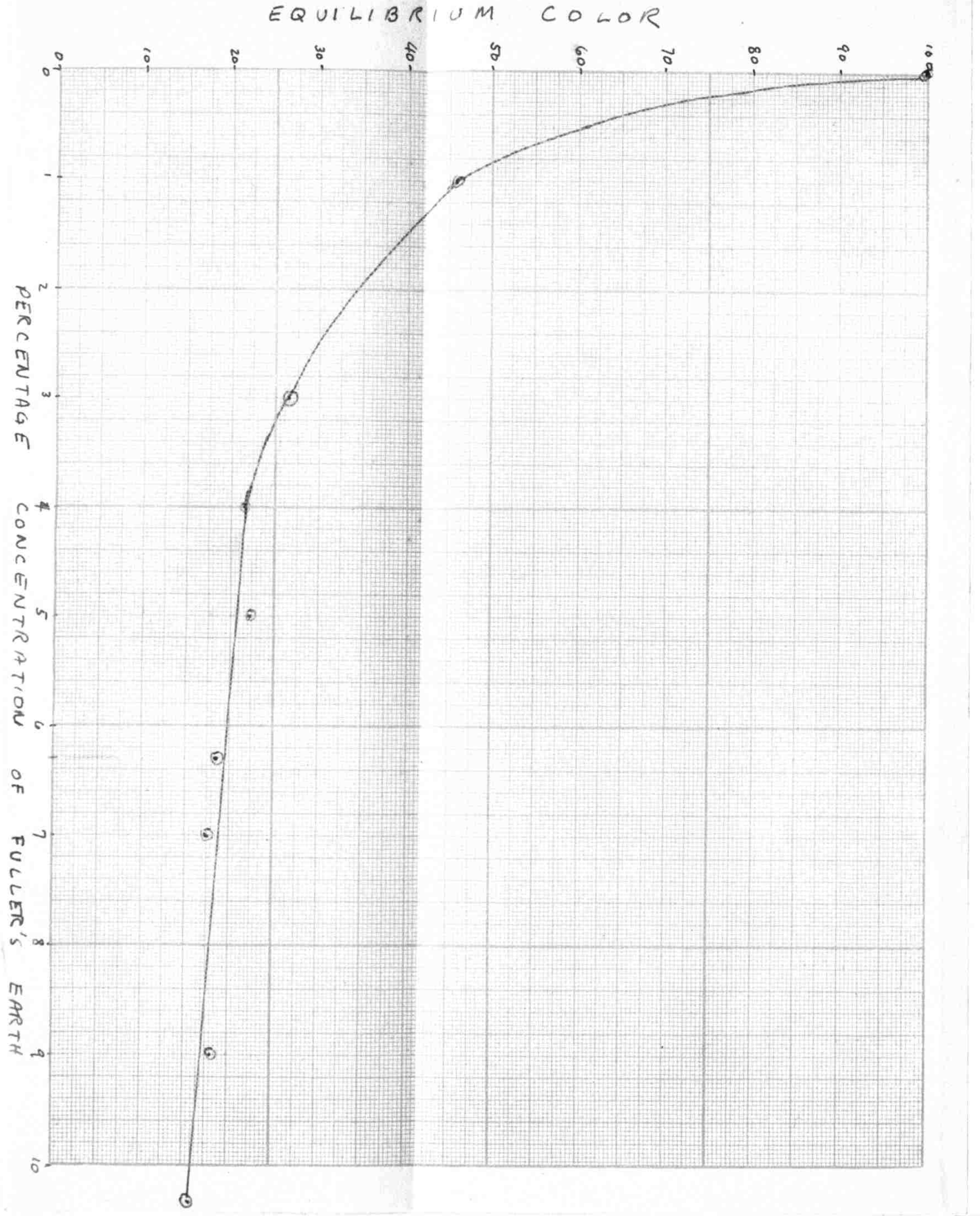
It can be seen that a straight line (the broken line) can easily be passed through the upper three points, corresponding to concentrations of 1, 3, and 4 percent of the earth, and this line curves as it passes through the other points. Kulkarni and Jatkar (40) obtained similar results with safflower oil having a Lovibond color value of 16.7 yellow. The color removed was proportional to the weight of the earth only in the lower proportions. The curve was not linear throughout the whole range, but only in the lower concentrations. Hence they concluded that physical adsorption appears to predominate at low concentrations and chemical adsorption at higher concentrations, possibly with exchangeable H of the earth.

This could possibly account for the monlinear nature of the curve. If we take the first three points and pass a straight line and find the intersection of this line with the ordinate $c = 1$ the following values are obtained:

$$k = 0.3 \quad \text{and} \quad n = 1.35$$

These values should be taken as the more accurate, as it is within this range that physical adsorption occurs only, and also because


EQUILIBRIUM COLOR
0
10
20
30
40
50
60
70
80
90
100
PERCENTAGE CONCENTRATION OF FULLER'S EARTH
0
1
2
3
4
5
6
7
8
9
10


EQUILIBRIUM COLOR
0
10
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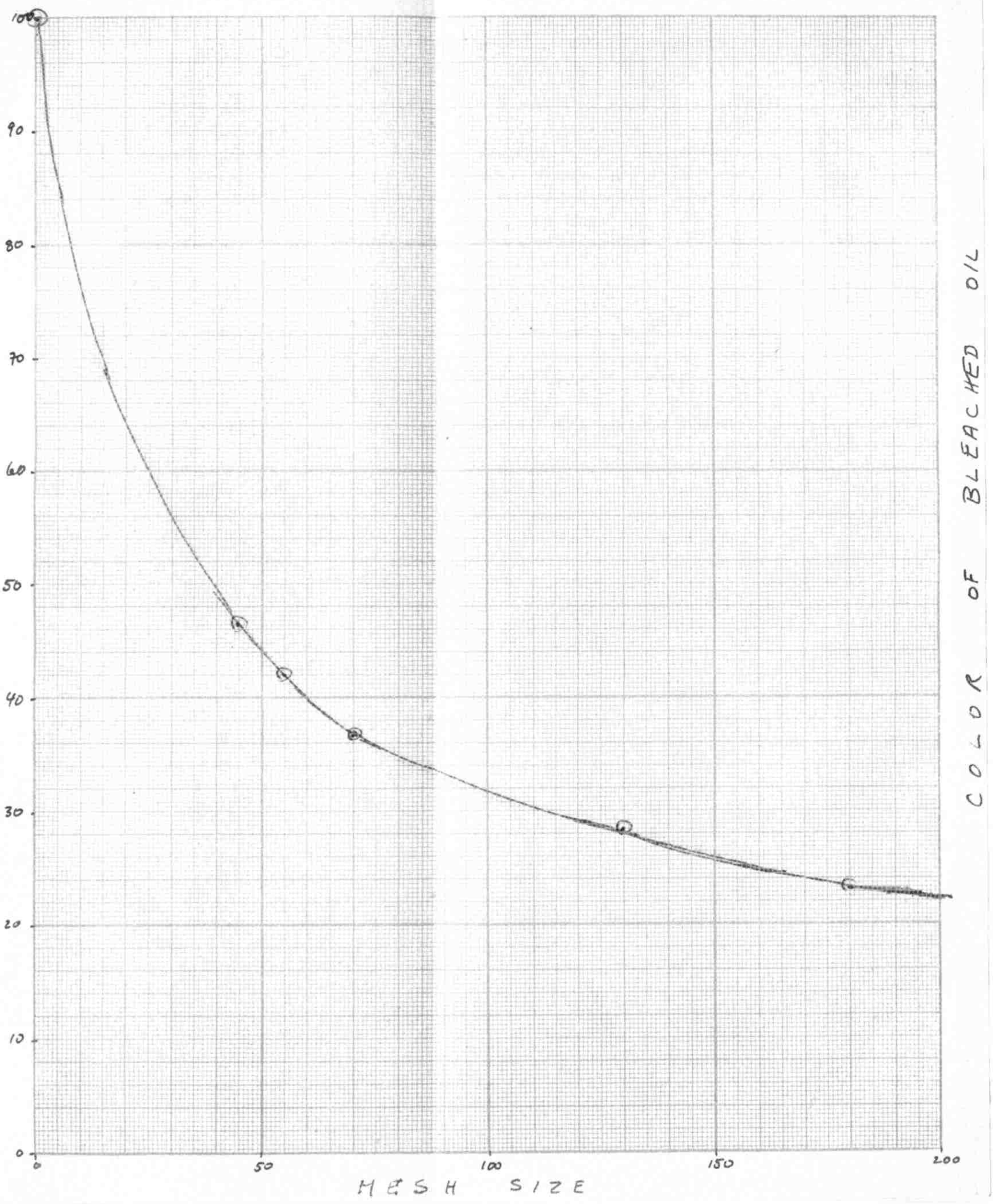
30
40
50
60
70
80
90
100
PERCENTAGE CONCENTRATION OF FULLER'S EARTH
0
1
2
3
4
5
6
7
8
9
10

in actual practice the earth is not used at a concentration of more than 4 to 5 percent.

It was intended to use the Red Lovibond color units, instead of assigning arbitrarily a value of 100 to the standard. The color of the standard unbleached oil was 10 yellow and 0.8 red Lovibond units. This would give very small figures for the red color units for the bleached oils. So the former method was preferred. It can be shown, however, that the values of k and n are independant of the units used for measuring the color of pigment concentrations.

The graph on the opposite page is obtained by plotting equilibrium color C against concentration of the earth. A 5 % concentration of the earth removes about 80 % of the color, while a 10 % concentration removes less than seven percent more of the color. So the earth is used most efficiently in proportions not more than 5 %.


100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
MESH SIZE
COLOR OF BLEACHED OIL

Section XIII - PRETREATMENT OF THE LOCAL EARTH

A. Mesh Size

We wanted to find out the relationship between mesh size and bleaching power of the local fuller's earth. The earth was ground and the following mesh sizes were taken: 40-50, 50-60, 60-80, and 80-180. Scieves with these meshes were the only ones found in the laboratory. The following is a table showing the average readings and the color at different mesh sizes:

Mesh Size	Average Duboscq Readings Standard Set at 5.0 mms.	Color, as compared with standard 100 units
40-50	10.78 mms.	46.4 units
50-60	11.90	42.0
60-80	13.57	36.8
80-180	17.67	28.3
passing 180	21.67	23.1

In graphing the above results, the average mesh was taken to be the middle of the range. The graph is shown on the opposite page.

As we have shown in section V, bleaching power increases with decrease of the size of particle, up to a certain point, where further decrease in size ruptures the pores of the particle. This according to Vollertsen occurs beyond 200 mesh (29). Therefore if we could go to finer meshes, we would expect the curve to rise again, so that a

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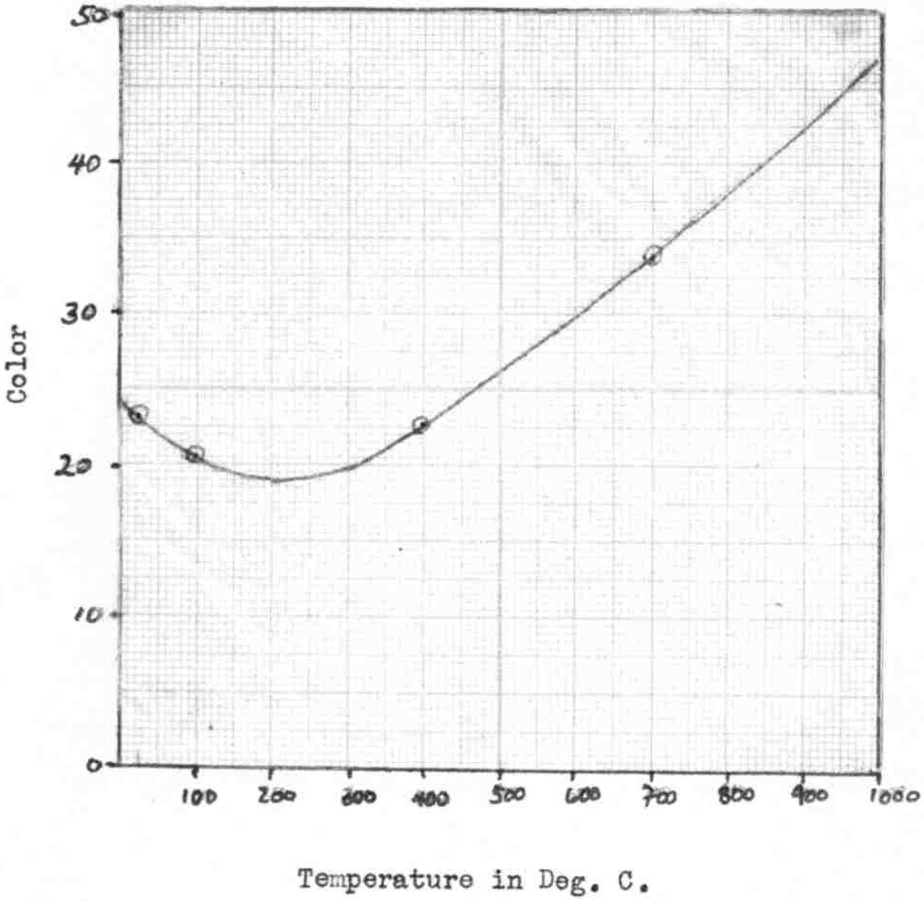

The Effect of Heating the Local Fuller's Earth on the Color of the Bleached Oil minimum color will be obtained corresponding to a maximum bleaching power.

B. Heat Treatment

As has already been seen in section V, heating raw fuller's earth will increase its activity, but further heating will decrease it. In constructing the following table, 10 g. portions were heated in an electric furnace for two hours. The earth was previously passed through 180 mesh. The temperature of the oven was controlled manually and variations in the temperature were a maximum of ± 20 deg. It was interesting to note that the local earth developed a deeper red color, the higher it was heated; this being due to the oxidation of the iron present. The results are shown in the following table:

Temperature deg. C.	Average Reading in Duboscq, Standard set at 5.0 mms.	Color, with the Standard [illegible] to 100 units
25	21.67 mms.	23.1 units
100	24.28	20.6
400	21.93	22.8
700	14.79	33.8

From the graph on the opposite page, we see that a minimum color or maximum bleaching is obtained upon heating to about 200 deg. C., the range being 150 to 250 deg.

Section IVX

ACTIVATION OF FULLER'S EARTH

Activation of the local fuller's earth was made as follows: One hundred grams of coarse granules of the earth were mixed with water to form a paste. 125 cc. of 3 M sulfuric acid were added and then about 100 ccs of water to generate steam. The whole was boiled in a round bottom flask to which a water cooled condensor was attached. The earth was heated for two hours, during which the temperature did not rise above 105 - 110 deg. C.

The earth was then filtered and washed free of acid. Six washing were necessary to completely remove the acid. The washed earth was then dried overnight at 105 deg. and then ground and passed through 180 mesh.

Four samples of oil were bleached, one with the English fuller's earth, another with the local fuller's earth untreated, but passing through 180 mesh, a third with activated local earth, dried at 105 deg., and a fourth with acivated local earth heated to 400 deg. Bleaching was done as described in section IX. The results are as follows:

Clay	Reading with standard set at 5.0mms.	Color, Standard =100 units
English fuller's earth	27.39 mms.	18.22 units
Local earth, untreated	25.53	19.59
Local earth activated and heated to 105 deg.	25.94	19.27
Local earth activated and heated to 400 deg.	24.56	20.26

In comparing the values obtained above, it should be remembered that the above results were obtained from experiments on the second sample of oil. Different samples of the same kind of oil, refined in the same way, may bleach differently.

From the above results we see that acid treatment of the local fuller's earth has no appreciable effect on the efficiency of the clay. This is to be expected since the earth is high in silica content. The ratio $SiO_2 : Al_2O_3$ is 5.00 which is a high value and according to King (3) the clay is of the unactivable type.

Part D.

Summary and Conclusion

SUMMARY AND CONCLUSION

In conclusion, the clay commonly called "keel" obtainable from Azas near Aleppo has good bleaching properties and can be used for bleaching oils and waxes. This local fuller's earth is comparable with the good English earths. The English fuller's earth removed 80.4 % of the color in a sample of cottonseed oil, while the local earth removed 76.9 %.

Chemically the local clay is high in silica content and according to King, is of the unactivable kind. It is of an average density, high in volatile matter and is neutral. Its values of the constants of Freundlich's isotherm are,

$$k = 0.3 \text{ and } n = 1.35$$

These being true when the earth is used in low concentrations. The above values mean that the earth is most efficiently used in successive stages, the concentration in each stage not exceeding 5 % of the weight of the oil.

The local fuller's earth shows increase in efficiency with increase of mesh size down to 180 and even lower. It is not worth activating the earth, as the increase in the efficiency is negligible, but the best treatment is to heat the raw earth up to 200 deg. for two hours.

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