ACTIVATION OF
SOME TURKISH CLAYS TO BE USED
IN BLEACHING OF EDIBLE OILS

A Thesis Submitted to the Graduate
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I - INTRODUCTION

The use of adsorbent or " bleaching " clay to refine oils and fats is as old as industry itself. In the terminology of the oil industry, bleaching clays are the natural clays and those that have been artificially activated by acid treatment.

Although a general procedure for acid-treatment of clays has been described by Mantel (1), Burghardt (5) and Kalichevsky (6), relatively little has been published concerning the procedure of activation of clays and the changes which occur in the clay structure during acid treatment.

The present investigation was directed towards the preparation of clays which would selectively adsorb coloring matter and impurities from " pirina" oil, which was obtained from Edremit. The term activity refers to this property of clays.

" Pirina" is the kind of oil which is obtained by extracting the traces of oil in olive seeds which were previously pressed for their oil content. The pirina oil is very dark green in color.

This research was done at the chemical engineering laboratories of Robert College. Attempts were made to activate clays from different regions of Turkey. These regions are Kütahya (Kunderen), Eskişehir (Çukurören), Eskişehir (Kıllıktepe), Kastamonu (Aptalhasan Village).

Clays were activated by making use of different methods. Clay activation depends on ten factors. Seven of them were varied while the remaining three factors were kept constant all the time.

The "pirina" oil was bleached using the activated clays by two different methods :

a- Direct method
b- Hexane method

The degree of activation of clays was measured by

a- Methylene-blue bleaching
b- Spectrophotometric transmission method

In order to prove the validity of some of the activation theories, analyses of clays , before and after the activated state, were made. Along this line, X-ray diffraction patterns of the clays were determined and crystal structure of the clays was identified. Using crystal diffraction patterns, some of the activation theories were disproved.

The best results were obtained with the clay from Kutahya, Emet-Kunderen, using hydrochloric acid as the activating acid. The crystal structure of this clay was found to be a mixture of Halloysite hydrated (endellite) $AlSi_2O_5(OH)_4 \cdot 2 H_2O$ and Oligoclase $0.83 \ NaAlSi_3O_8$, $0.16 \ CaAl_2Si_2O_8$.

II - THEORETICAL BACKGROUND

The most common bleaching clay is fuller's earth. Its name is derived from its early use in fulling, the operation of removing grease from woolen goods. Mantell (1) believes that fuller's earth and all adsorbent clays have their origin in the weathering of igneous rocks. The mass resulting from this weathering is chiefly magnesium - aluminum silicate in which traces of the original rocks remain in various stages of decomposition. The silicates which form fuller's earth are present as the minerals attapulgite, montmorillonite, vermiculite, kaolinite and halloysite. Grim (2) gives excellent theories on the crystalline structure of clay minerals and their relation to activation.

Decolorizing clays are usually those carrying Ca^{++} or Mg^{++} as exchangeable cations. But the fuller's earth itself must be important, because good decolorizing clays cannot always be prepared by a simple ion-exchange reaction and chemical composition of a particular clay bears no apparent relation to activity.

According to Grim (2), a clay should be crystalline in nature to be activated. Therefore, X-ray diffraction patterns or electron micrographs of clays have to be determined before starting any activation process.

X-Ray Analyses of Clay Minerals

X-rays are produced when electrons which have been accelerated by an electrical field, strike atoms usually in a solid target. As a result of electron bombardment of the target, electrons in inner orbits are displaced and the energy liberated, when electrons make the transition from a higher energy level to the vacancy in the inner orbit, is given out in the form of an X-ray photon. These transitions produce characteristic lines in the X-ray spectrum. Although X-rays are diffracted by the crystal lattice just as visible light is diffracted by gratings, it is pointed out that it is convenient to consider that the X-rays are reflected from planes in the crystal.

A simple relation exists between the wavelength of the X-rays, the distance between the planes in the crystal and the angle of reflection . The equation, which is called the Bragg equation may be derived in reference to Figure 1 .

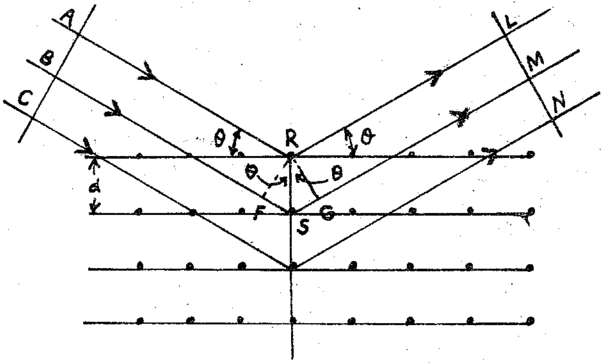


Fig. 1 Diagram used in proving $n\lambda = 2d \sin\theta$

The horizantal lines represent layers in the crystal separated by the distance d. Using this figure one can obtain the following formula:

$$n\lambda = 2d \sin\theta$$

The equation gives the relationship of the distance between planes in a crystal and the angle at which the reflected radiation has a maximum intensity for a given wavelenght λ.

Diffraction Methods Used

Three principal diffraction methods are used in X-ray crystallography:

	λ	θ
Laue Method	variable	fixed
Rotating Crystal Method	fixed	partly variable
Powder Method	fixed	variable

Laue Method

Polychromatic or white X-rays are passed through a carefully oriented crystal which is mounted a few centimeters in front of a photographic film. Laue method is in itself of two parts:

a- Transmission Method
b- Back-reflection Method

In transmission method, (33) the film is placed in front of the crystal. Thus, diffracted rays are photographed on the film.

In back reflection method, the film is placed between X-ray source and the crystal. First, X-ray passes through a hole in the film, strikes the crystal, is diffracted and then the back diffracted rays are recorded on the film .

Rotating Crystal Method

In this method, one crystal (33) is placed in such a way that one of its main axis is perpendiculer to the incoming X-ray A cylindrical film is placed around the crystal. The crystal is rotated around its axis. In the meantime lattice planes of the crystal will make reflections in accordance with the Bragg angle, and these will be recorded on the film.

Powder Method

Instead of scattering X-ray from a single large crystal, it is convenient in some types of work to pass a beam of X-rays through a large number of small crystals oriented in random directions. The reflection may be recorded on a circular photogaphic film as in Figures 2 and 3 .

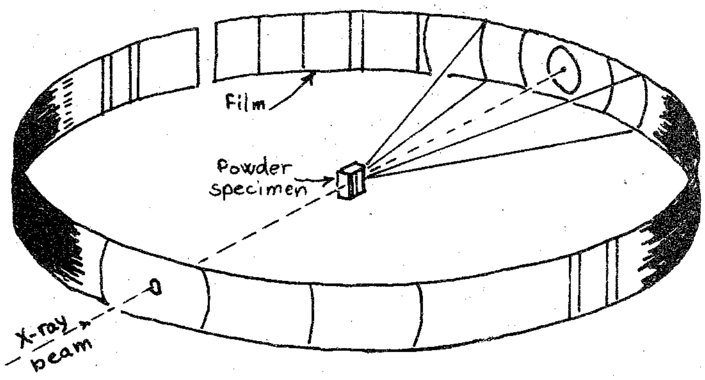


Fig 2. X-ray powder camera

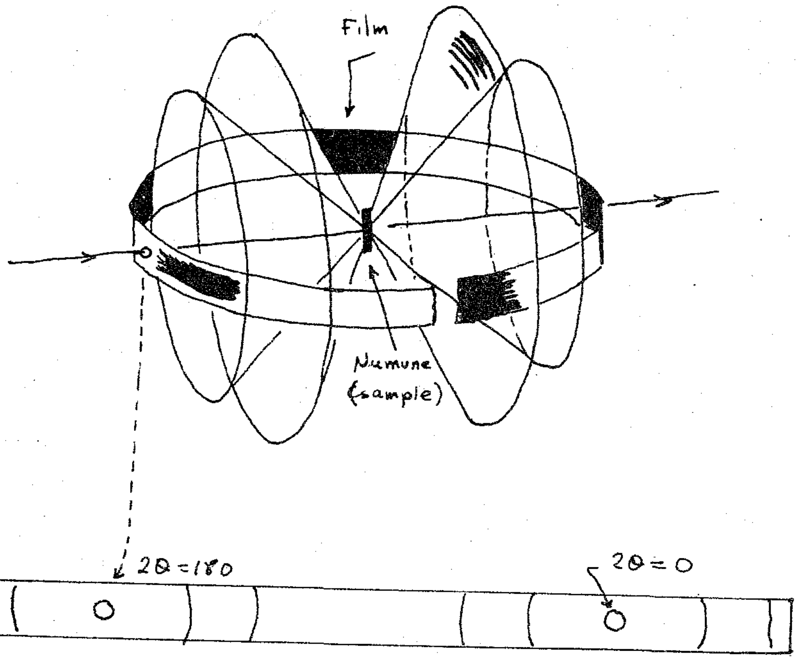


Fig 3. Debye - Scherrer powder method

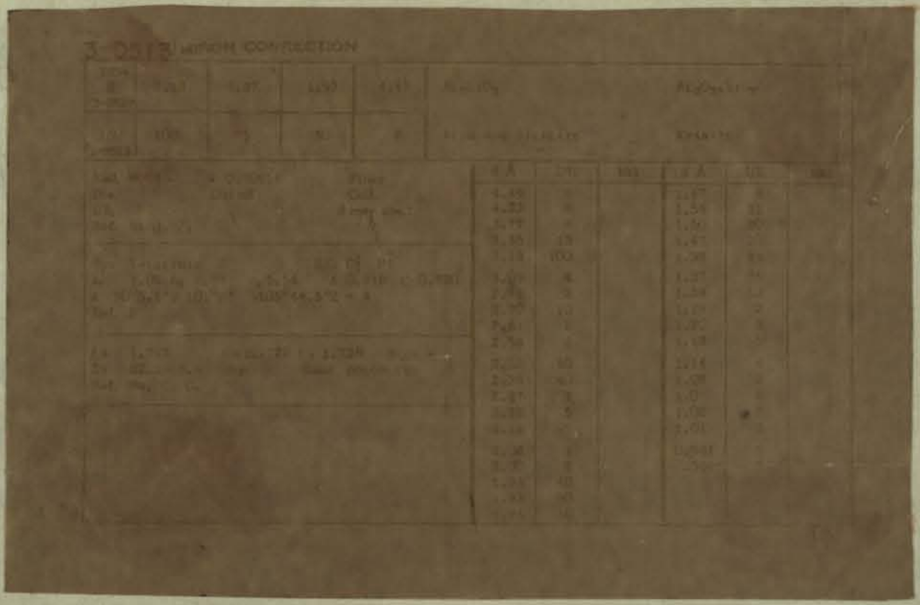
Clay minerals exist for the most part in very fine particles and powder method (2) must be used to obtain the diffraction data.

Identification of a Material Using Powder method

The material which is to be identified gives a characteristic diffraction pattern. The sample may be a mixture or pure. The diffraction pattern (33) is as distinct as the finger print, but how can one identify the sample using its diffraction pattern? If one has diffraction patterns of many materials, the identification of an unknown becomes easy and is a matter of comparison only.

In 1939 Hanawalt (32) made such a collection of diffraction patterns of materials . In powder method, diffraction patterns are identified by 2 θ values and the intensities of the diffracted rays, but 2 θ values depend on wavelenth of X-rays. Since d values are fixed for constant wavelength , Hanawalt used intensity I and d values in comparing diffraction patterns with his standards. Hanawalt collected diffraction patterns for about 1000 known materials. This number was later increased by the American Society of Testing Materials. In 1955, 5900 standard diffraction patterns were published. Most of the published patterns belong to inorganic compounds.

More than one compound may have the same or close d_1 values. (d_1 value corresponds to the distance in planes which reflects most intensely.) Therefore to identify a material Hanawalt used d_1, d_2, and d_3 values and the corresponding intensity values. A typical standard of American Society of Testing materials , ASTM is given below:



The d values which appear at the left-upper corner represent the most intense lines in the diffraction pattern. Namely, 100,75, and 50 % intense lines. The number 3-0513 corresponds to the place of this card in the ASTM group.

It is rather difficult to identify an unknown sample directly from ASTM cards. Therefore an auxilary book named Hanawalt index (32) is used simultaneously . The procedure to identify an unknown crystal material is given later in the section regarding the experiments.

Theory of Activation and Bleaching

Activation Theories:

The term "activation" of clay material with acid treatment is rather difficult to describe. Various authors define it differently and sometimes contradict each other.

Alexander (8) defines activation with acid treatment as removing alkalies, alkaline earths, some of the alumina and leaving a residue of very fine grains of aluminum silicate. Nagornaya (11) and Puri (21) assert that treatment of clay samples with hydrochloric acid at 100°C reduces the content of Al_2O_3, Fe_2O_3, alkali oxides, alkali earth oxides and increases the $SiO_2:Al_2O_3$ ratio.

According to Crepar (10), structure change in montmorillonite clays is the activation. Specific surface is increased by the formation of the hydrated silica which in turn breaks the bonds of the montmorillonite. This theory is also supported by Komarov (12). Komarov suggests that after activation with hydrochloric acid, the crystal lattice of montmorillonite is destroyed and only relics of the original mineral remain.

Mills (19) visualizes the activation by acid treatment as occuring by attack from the edges of the montmorillonite lattice structure and proceeding by leaching out the basic constituents to leave ultimately a silica skeleton. It is beleived by Mills (19) that the "inactivable" bentonites were so constituted that they lost most of their alumina content during acid treatment and became more nearly pure silica.

Morita (15) found no noticeable correlation between chemical composition of clays and their capacity to activation, but he found a relation between the activation and the concentration of the activating acid. Alexanian (22) thinks that preliminary knowledge of the crystallographic structure of a clay is the most important factor in determining its capacity to activation and the activation procedure. A clay should have a crystalline structure to be activated. Alexanian (22) illustrates the complexity of the problem with the following two clays: a clay from Germany which cannot be activated and an easily activable Maraccon montmorillonite were almost identical in chemical composition.

Organic acids do not have nearly the power of mineral acids to activate bleaching earths. The reason for this fact is explained by Weldes (27). He made comparative analyses of earths treated with a mineral acid and tartaric acid. The content of Al_2O_3 in the resulting product from the treatment with tartaric acid was high.

Theories formulated before 1950 rely on H_2O content. For example in 1947, Kazuhiko (18) stated that adsorption activity (which is the bleaching action of clays) depended on H_2O content and earths containing hydrated Fe oxide or Fe oxide should have higher activities. The same thing is also asserted by Ross (20) in 1948. He wrote that the declorizing capacity of any given clay increased as its absorbed H_2O content decreased.

Bleaching Theories

According to Ries (3), the phenomenon of bleaching is one simple adsorption. This indicated by the fact that an earth which has taken up all the color it will hold, yields all of its color to alcohol after the adhering oil has just been extracted with ether or gasoline.

Investigations of clay materials in many different fields for many years have produced evidence of some kind of a reaction between the fundamental components of clay and organic material. Since the early 1930's a large amount of work has been done on this problem and the character of clay-mineral-organic reactions has now been fairly well established. The early work of Hofmann (40) in 1934 and that of Myers (41) suggested that organic compounds with polar active groups would be adsorbed by the clay minerals. Bradley and Mac Evan (35) at about the same time quite independeantly, showed definitely that the nonionic organic molecules of polar character could be adsorbed by the clay minerals. Heindricks (42) indicated that organic ions are held by Van der Waals forces in addition to the coulombic force. In general the larger ions are more strongly adsorbed beacuse of the greater Van der Waals forces. Grim, Allaway and Cuthbert (43) have shown that small ions are adsorbed only up to the cation-exchange capacity, whereas larger ions are adsorbed by Van der Waals forces and these forces are supplemented by O - H -------O bonds between the organic molecule and the clay-mineral surface.

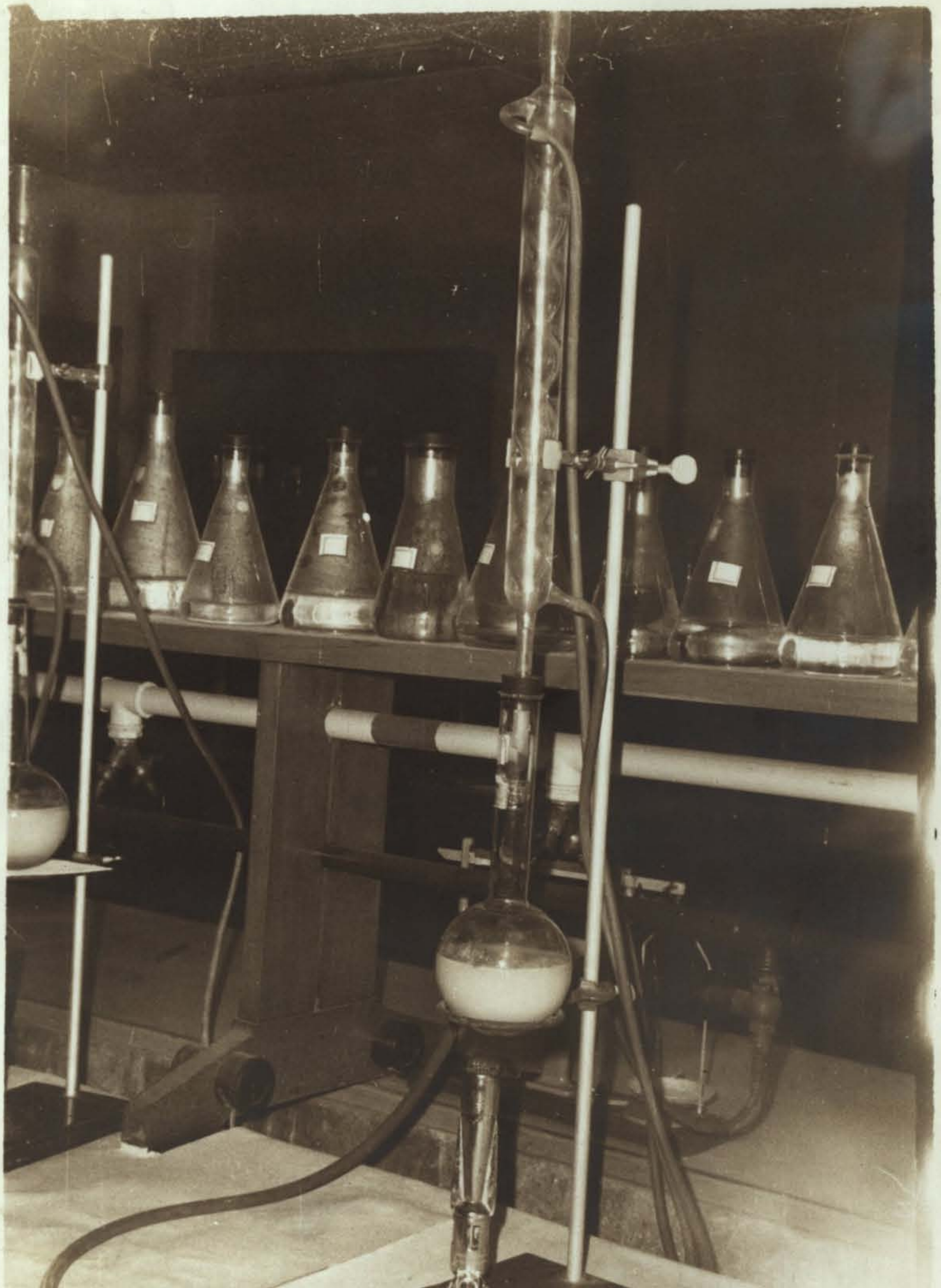


Fig. 4. The Reflux System

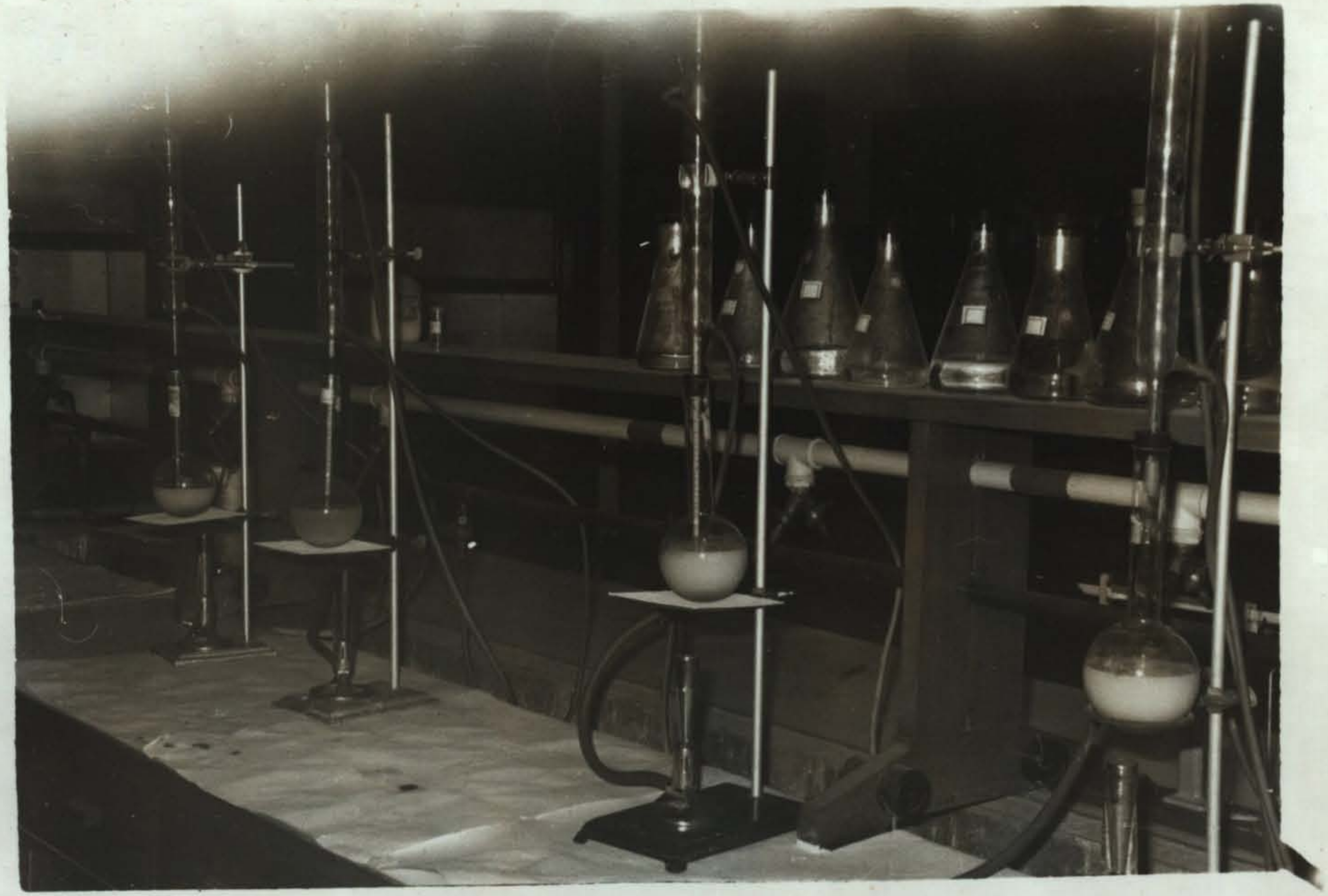


Fig. 5 The Reflux System

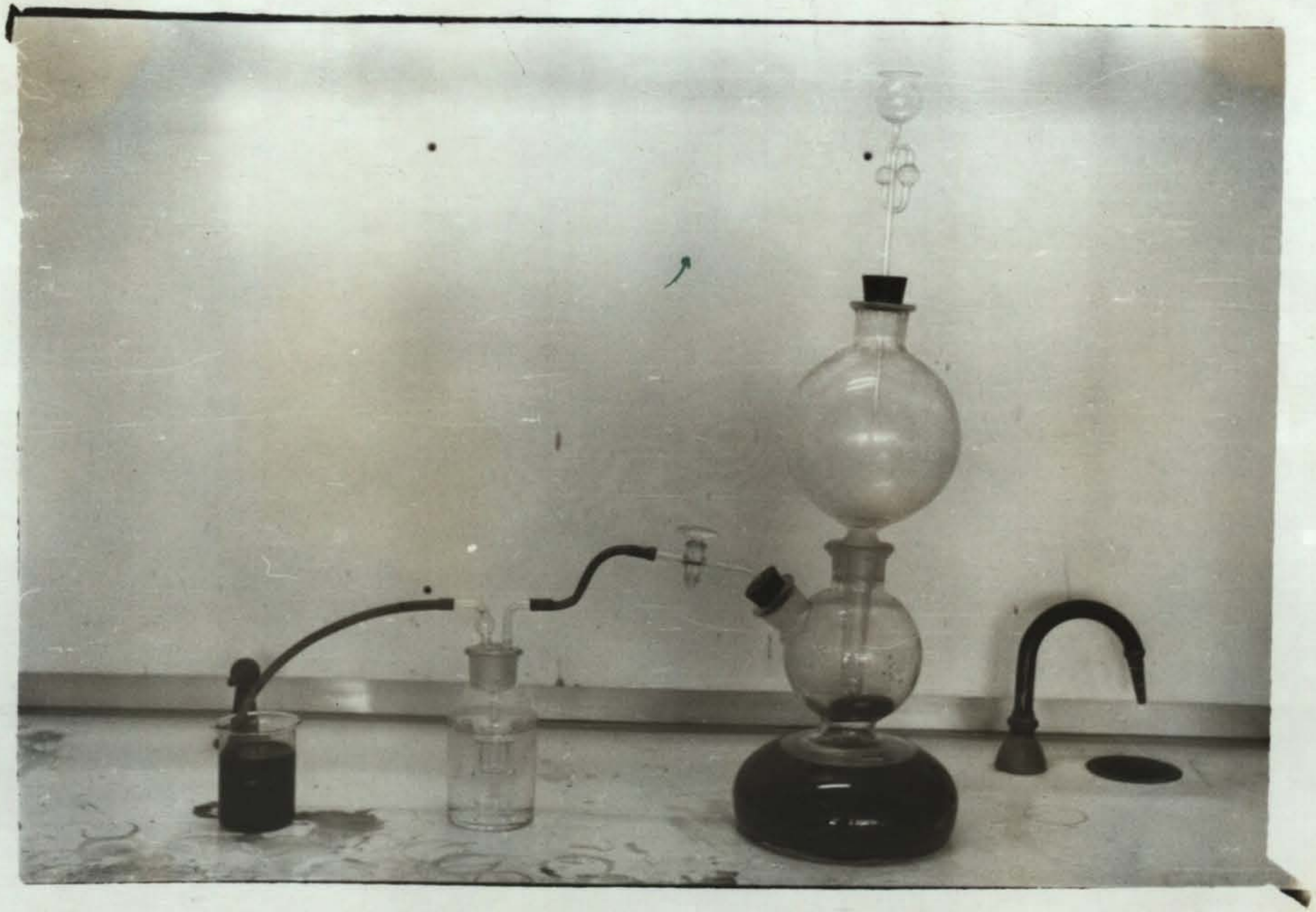


Fig. 6. Equipment for Obtaining H_2S

III

EXPERIMENTS

The experimental work can most conveniently be presented by describing separately (a) the experimental apparatus, (b) the materials used and (c) the experimental procedure.

a) <u>Experimental Apparatus</u>

The main components of the apparatus are:

1) Reflux system composed of a reflux condenser, a 750 ml. reflux bottle and a thermometer as shown in Figures four and five.
2) Equipment for obtaining H_2S (to be used in clay analysis) as indicated in Figure six.
3) Grinder and powderizers
4) Safety-Head centrifuge with underguard and safety cap. A.C. operated at 4275 rpm.
5) Electric-oven, operated at 105°C.
6) Zeiss-Spectrophotometer.
7) X-ray producer utilizing a copper tube.

b) <u>Materials Used</u>

1) Five types of clays were used in this work. They were obtained from the locations indicated below:

Kütahya - Emet (vicinity of Halifeler)
Eskişehir - Kıllıktepe (Başören)

Eskişehir - Mihalıççık (Çukurören)
Kastamonu - Taşköprü
Kastamonu - Aptal Hasan

These clays will be referred to as C_1, C_2, C_3, C_4 and C_5 respectively

2. Pirina oil
3. Standard bleaching earths named as "Fulmond grade A-A" and "Red Hill-Surrey KN 11 C"
4. H_2SO_4 (concentrated and pure)
   HCl (concentrated, 37 percent by weight and pure)

c) Experimental Procedure

The experiments of this work can be classified as:

A) Activation Experiments
B) Bleaching Experiments
C) Degree of Activation measurements
   Methylene Blue Method
   Spectrophotometer method
D) X-ray Experiments
E) Different Methods of Bleaching
F) Chemical Analysis of Clays

A) Activation Experiments

Activation of clays depends on the following factors:

1) clay
   a) type
   b) moisture present
   c) particle size - hence pore size and surface area
   d) pH

2) Acid
    a) type
    b) concentration
3) time
    a) of activation
    b) of drying of activated clay
4) Temperature
    a) of activation
    b) of drying of activated clay

The activation experiments were carried out by changing one variable while keeping the others constant as indicated in Table I.

All the experiments were performed using the same experimental method. This method is described as follows:

The five types of clays are ground to powder size, sieved through 0.25 mm. openings and dried at 100°C for one hour.

In each of the five reflux bottles 30 gm of clay, 75 ml of distilled H_2O and a certain concentration of acid were mixed. The ingredients were refluxed for a certain time at 105°C. Then the system was cooled and allowed to settle down in a 600 ml beaker for about 30 minutes. A two layered solution and a residue were obtained. One layer of the solution constituted the dissolved alkalies in the clay and the other layer was excess acid. After pouring off the solution, the residue in the beaker was washed to neutrality or to a certain pH value. Then it was filtered using a Büchner funnel and a vacuum pump. The residue was then dried in the oven at a certain temperature for three hours. The dried material was ground to powder size and sieved through 0.25 mm. openings and kept in a desicator. All of the activation experiments are shown in Table I.

B. Bleaching Experiments

The results of a bleaching experiment depend on the following factors:

1) Method used for bleaching
2) Contact time of bleaching
3) Stirring of the oil
4) Bleaching temperature
5) Amount of clay used
6) Type of the material to be bleached

In these experiments, the last three variables were held constant.

Bleaching Method 1

One hundred grams "pirina oil" were weighed into a 100 ml. beaker. It was heated to 90°C in the oven and 2 gm of activated clay were added. To maximize bleaching efficiency, the sample was stirred almost continuously. The bleaching was continued for 40 minutes. Samples were taken at the end of 25 and 40 minutes. In order to eliminate its bleaching effect, the bleached oil was not filtered through a filter paper. Instead, the samples are centrifuged. The clay settled down to the bottom and the clear oil was transfered to a clean, labeled test tube. For the active clays, the residue at the end of the centrifuge process was a black, greasy substance. For the nonactive clays, the residue maintained the original color of the clay and the clay particles were distinct.

Bleaching Method 2

Everything was the same as the above procedure with the exception that the oil and the clay were mixed and then heated to 90°C. This method was applied to the 30% and 40% HCl activated C_1 clay.

C. Degree of Activation Measurements

I) Spectrophotometer method

To find out the correct value of the wavelength of the monochromatic sodium light, λ, a series of transmittance trials were run on the standard oil sample. The results are tabulated in Table II and are presented graphically in Figure 14.

At the start of the investtigation, the England-Import "Fulmond Grade A-A" and "Red-Hill, Surrey KN 11 C" bleaching earths were considered as the most active clays. Hence the pirina oil samples bleached with these clays were considered as standards for the degree of activation measurements. However, later on, it was found that "Fulmond Grade A-A" was superior in bleaching ability to "KN 11 C" . The ratio of transmittance for the oil bleached by the "Fulmond A-A" and the "KN 11 C" was 100 to 88 respectively. Therefore, all measurements in this work were based on "Fulmond Grade A-A" clay.

TABLE I

Experiment Number	Type of Clay	Type of Acid	Conc. of Acid %w	pH of Activated Clay	Time of Activation hr	Drying Time hr	Drying Temperature C°	Particle Size (mm)	Moisture Present %	Activation Temperature C°
I	C_1-C_5	HCl	20	7	3	3	120	0.25	10	105
II	C_1-C_5	HCl	30	7	3	3	120	0.25	10	105
III	C_1-C_5	HCl	40	7	3	3	120	0.25	10	105
IV	C_1-C_5	HCl	50	7	3	3	120	0.25	10	105
V	C_1-C_5	HCl	60	7	3	3	120	0.25	10	105
VI	C_1-C_5	H_2SO_4	30	7	3	3	120	0.25	10	105
VII	C_1-C_5	H_2SO_4	30	7	6	3	120	0.25	10	105
VIII	C_2	H_2SO_4	34	7	6	3	120	0.25	10	105
IX	C_2	H_2SO_4	34	6	6	3	120	0.25	10	105
X	C_2	H_2SO_4	38	7	6	3	120	0.25	10	105
XI	C_2	H_2SO_4	38	6	6	3	120	0.25	10	105
XII	C_1	HCl	31	6	3	3	120	0.25	10	105
XIII	C_1	HCl	32	6	3	3	120	0.25	10	105
XIV	C_1	HCl	33	6	3	3	120	0.25	10	105
XV	C_1	HCl	34	6	3	3	120	0.25	10	105
XVI	C_1	HCl	36	6	3	3	120	0.25	10	105

TABLE I continued

Experiment Number	Type of Clay	Type of Acid	Conc. of Acid %w	pH of Activated Clay	Time of Activation hr	Drying Time hr	Drying Temperature C°	Particle Size (mm)	Moisture Present %	Activation Temperature C°
XVII	C_1	HCl	31	7	3	3	120	0.25	10	105
XVIII	C_1	HCl	32	7	3	3	120	0.25	10	105
XIX	C_1	HCl	33	7	3	3	120	0.25	10	105
XX	C_1	HCl	34	7	3	3	120	0.25	10	105
XXI	C_1	HCl	36	7	3	3	120	0.25	10	105
XXII	C_1	HCl	37	7	3	3	120	0.25	10	105
XXIII	C_1	HCl	42	7	3	3	120	0.25	10	105
XXIV	C_1	H_2SO_4	33	7	6	3	120	0.25	10	105
XXV	C_1	H_2SO_4	33	6	6	3	120	0.25	10	105
XXVI	C_1	HCl	31	6	3	3	160	0.25	10	105
XXVII	C_1	HCl	32	6	3	3	160	0.25	10	105
XXVIII	C_1	HCl	33	6	3	3	160	0.25	10	105
XXIX	C_1	HCl	34	6	3	3	160	0.25	10	105
XXX	C_1	HCl	36	6	3	3	160	0.25	10	105
XXXI	C_1	HCl	31	7	3	3	160	0.25	10	105
XXXII	C_1	HCl	32	7	3	3	160	0.25	10	105
XXXIII	C_1	HCl	33	7	3	3	160	0.25	10	105
XXXIV	C_1	HCl	34	7	3	3	160	0.25	10	105
XXXV	C_1	HCl	36	7	3	3	160	0.25	10	105

Table II

% Transmittance versus wave length

$\lambda (m\mu)$	% Transmittance	$\lambda (m\mu)$	% Transmittance
400	0.00	580	30.05
410	0.00	590	24.50
420	0.00	600	14.00
430	0.00	610	10.00
440	0.00	620	7.50
450	0.00	630	5.00
460	0.00	640	3.00
470	1.40	650	2.00
480	3.00	660	1.00
490	5.40	700	0.00
500	8.00	710	0.00
510	11.00	720	0.00
520	15.00	730	0.00
530	18.50	740	0.00
540	22.00	740	0.00
550	23.78	750	0.00
560	26.50	750	0.00
570	29.50	760	0.00

Spectrophotometric Results

Table 1

$\lambda = 580\ m\mu$

Sample Taken at 25 minutes

20% HCl

Type of Sample	% Transmission Right After Bleaching	% Transmission Two Months After Bleaching
C_1	20	30
C_2	25	35
C_3	20	30
C_4	10	20
C_5	10	15

TABLE 2

$\lambda = 580$ mμ

20% HCl. Sample Taken at t= 40 minutes

Type of Sample	% Tramsmission Right After Bleaching	% Transmission Two Months After Bleaching
C_1	25	30
C_2	27	31
C_3	23	25
C_4	10	12
C_5	10	12

Table 3

$\lambda = 580$ mμ

Sample Taken at t= 25 minutes

30% HCl

Type of Sample	% Transmission Right After Bleaching (abbreviated to RAB)	% Transmission Two Months After Bleaching (abbreviated to 2 MAB)
C_1	35	40
C_2	30	40
C_3	20	30
C_4	10	12
C_5	10	12

Table 4

$\lambda =$ 580 mμ

Sample Taken at t= 40 minutes

30% HCl

Types of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	37	42
C_2	32	45
C_3	20	30
C_4	10	12
C_5	10	12

Table 5

λ = 580 mμ

Sample Taken at t= 25 minutes

40% HCl

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	40	45
C_2	30	32
C_3	25	30
C_4	10	10
C_5	10	10

Table 6

$\lambda = 580\ m\mu$

Sample Taken at t= 40 minutes

40% HCl

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	42	47
C_2	30	35
C_3	30	33
C_4	10	12
C_5	10	12

Table 7

$\lambda = 580\ m\mu$

Sample Taken at t= 25 minutes

50% HCl

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	25	30
C_2	25	30
C_3	20	25
C_4	10	12
C_5	10	12

Table 8

$\lambda = 580$ m μ

Sample Taken at t= 40 minutes

50% HCl

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	27	32
C_2	30	33
C_3	22	25
C_4	10	12
C_5	10	12

Table 9

$\lambda = 580\ m\mu$

Sample Taken at t= 25 minutes

60% HCl

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	20	28
C_2	18	22
C_3	21	24
C_4	8	12
C_5	8	11

Table 10

$\lambda = 580\ m\mu$

Sample Taken at t= 40 minutes

60% HCl

Type of Sample	% Transmission R.A.B	% Transmission 2 M.A.B.
C_1	20	25
C_2	18	20
C_3	17	19
C_4	8	10
C_5	7	9

Table 11

$\lambda = 580\ m\mu$

Sample Taken at t= 25 minutes

30% H_2SO_4 Three Hour Activation

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	40	45
C_2	35	42
C_3	30	34
C_4	18	20
C_5	17	21

Table 12

$\lambda = 580\ m\mu$

Sample Taken at t= 40 minutes

30% H_2SO_4 Three Hour Activation

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	50	55
C_2	50	55
C_3	35	40
C_4	19	20
C_5	18	21

Table 13

$\lambda = 580\ m\mu$

Sample Taken at t= 25 minutes

30% H_2SO_4 Six Hour Activation

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	55	62
C_2	50	55
C_3	40	42
C_4	18	20
C_5	12	15

Table 14

$\lambda = 580\ m\mu$

Sample Taken at t= 40 minutes

30% H_2SO_4 Six Hour Activation

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	75	91
C_2	50	62
C_3	40	45
C_4	18	21
C_5	15	17

Table 15

λ = 580 mμ

Sample Taken at t= 25 minutes

34% H_2SO_4 Six Hour Activation

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_2(pH6)	50	61
C_2(pH7)	45	50

Table 16

λ = 580 mμ

Sample Taken at t= 25 minutes

38% H_2SO_4 Six Hour Activation

Type od Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_2(pH6)	41	48
C_2(pH7)	35	42

Table 17

$\lambda = 580$ mμ

Sample Taken at t = 25 minutes

58 % H_2SO_4 Six Hour Activation

Type of Sample	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_2 (pH 6)	41	48
C_2 (pH 7)	55	42

Table 18

$\lambda = 580$ mμ

Sample Taken at t = 40 minutes

58 % H_2SO_4 Six Hour Activation

Type of Sample	% Transmission R.A.B.	% Transmission 2.M.A.B.
C_2 (pH 6)	51	59
C_2 (pH 7)	48	55

Table 19

$\lambda = 580$ mμ

Sample Taken at t= 25 minutes

C_1 Three Hour Activation

Acid Concentration (H Cl)	% Transmission R.A.B.	% Transmission 2 M.A.B.
31% (pH 6)	38	42
31% (pH 7)	34	40
32% (pH 6)	38	45
32% (pH 7)	35	42
33% (pH 6)	40	50
33% (pH 7)	36	42
34% (pH 6)	45	55
34% (pH 7)	48	59
36% (pH 6)	60	75
36% (pH 7)	51	67

Table 20

$\lambda = 580$ m μ

Sample Taken at t= 40 minutes

C_1 Three Hour Activation

Acid Concentration (H Cl)	% Transmission R.A.B.	% Transmission 2 M.A.B.
31% (pH 6)	42	50
31% (pH 7)	38	45
32% (pH 6)	42	50
32% (pH 7)	39	44
33% (pH 6)	42	51
33% (pH 7)	40	47
34% (pH 6)	48	54
34% (pH 7)	52	60
36% (pH 6)	72	85
36% (pH 7)	60	71

Table 21

$\lambda = 580\ m\mu$

Sample Taken at t= 25 minutes

C_1 Three Hour Activation

Acid Concentration (H Cl)	% Transmission R.A.B.	% Transmission 2 M.A.B.
37% (pH 7)	76	85
42% (pH 7)	60	71

Table 22

$\lambda = 580\ m\mu$

Sample Taken at t= 40 minutes

C_1 Three Hour Activation

Acid Concentration (H Cl)	% Transmission R.A.B.	% Transmission 2 M.A.B.
37% (pH 7)	82	94
42% (pH 7)	62	74

Table 23

$\lambda = 580$ mμ

Sample Taken at t= 25 minutes

C_1 Three Hour Activation

Acid Concentration (H_2SO_4)	% Transmission R.A.B	% Transmission 2 M.A.B.
33% (pH 6)	68	78
33% (pH 7)	65	74

Table 24

$\lambda = 580$ mμ

Sample taken at t= 40 minutes

C_1 Three Hour Activation 160°C

Acid Concentration (H_2SO_4)	% Transmission R.A.B.	% Transmission 2 M.A.B.
33% (pH 6)	74	38
33% (pH 7)	69	72

Table 25

$\lambda = 580$ mμ

Sample Taken at t = 25 minutes

C, Three Hour Activation   Dried at 160°C

Acid Concentration HCl	% Transmission R.A.B.	% Transmission 2 M.A.B.
31 % pH 6	30	35
31 % pH 7	25	31
32 % pH 6	31	34
32 % pH 7	28	30
33 % pH 6	37	42
33 % pH 7	25	30
34 % pH 6	40	42
34 % pH 7	42	45
36 % pH 6	50	55
36 % pH 7	45	52

Table 26

$\lambda = 580\ m\mu$

Sample Taken at t= 40 minutes

C_1 Three Hour Activation (Dried at 160°C)

Acid Concentration (HCl)	% Transmission R.A.B.	% Transmission 2 M.A.B.
31% (pH 6)	31	35
31% (pH 7)	27	31
32% (pH 6)	34	34
32% (pH 7)	30	30
33% (pH 6)	38	42
33% (pH 7)	26	30
34% (pH 6)	40	42
34% (pH 7)	43	45
36% (pH 6)	51	55
36% (pH 7)	46	52

Table 27

$\lambda = 580$ mμ

Bleaching Method Two

C_1

Acid Concentration (H Cl)	% Transmission R.A.B.	% Transmission 2 M.A.B.
30%	20	25
40%	25	30

Table 28

$\lambda = 580\ m\mu$

Unactivated Clays

Type of Clay	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1	20	22
C_2	20	21
C_3	10	10
C_4	0	0
C_5	0	0

II- Methylene -Blue Method

This method of measurement is a method of color comparison. Seven samples of methylene blue solution are prepared.

1- 0.02 % by weight
2- 0.05 % "
3- 0.1 % "
4- 0.2 % "
5- 0.3 % "
6- 0.4 % "
7- 3.5 % "

The same amount of each of these solutions is placed in identical bottles of the same volume. They are used as standards for the comparison.

Procedure

The amount of 0.500 gm. of clay is placed onto No: 31 Whatman filter paper. The system is placed into a funnel, then 5 ml. of solution number seven is poured into it and filtered. The resulting filtrate is compared in color with identical amounts of the standard solution. The results of the experiment are tabulated in Tables 29-33

Table 29

Clay Type: C_1

Acid Concentration (H Cl)	pH of Clay	Number of the Standard Having Equivalent Color
31%	6	3
32%	7	3
33%	6	3
34%	7	2
35%	7	1
37%	7	1
42%	7	2
20%	7	4
30%	7	3
40%	7	4
50%	7	5
60%	7	6
35% H_2SO_4 (6 hr. act.)	7	1
Raw Clay		4

Table 30

Clay Type: C_2

Acid Concentration (H Cl)	pH of Clay**	Number of the Standard Having Equivalent Color
20%	7	4
30%	7	3
40%	7	4
50%	7	5
60%	7	6
35% H_2SO_4 (6 hr. act.)	7	2
Raw Clay		5

Table 31

Clay Type: C_5

Acid Concentration (H Cl)	pH of Clay	Number of the Standard Having Equivalent Color
20%	7	6
30%	7	6
40%	7	5
50%	7	7
60%	7	7
35% H_2SO_4 (3 hr. act.)	7	6
35% H_2SO_4 (6 hr. act.)	7	6
Raw Clay		6

Table 32

Clay Type C_4

Acid Concentration (H Cl)	pH of Clay	Number of the Standard Having Equivalent Color
20%	7	6
40%	7	6
50%	7	7
60%	7	7
35% H_2SO_4 (6hr. act.)	7	6
35% H_2SO_4 (3hr. act.)	7	6
Raw Clay		6

Table 33

Clay Type: C_3

Acid Concentration (H Cl)	pH of Clay	Number of the Standard Having Equivalent Color
20%	7	4
50%	7	7
60%	7	7
35% H_2SO_4 (3 hr. act.)	7	2
35% H_2SO_4 (6 hr. act.)	7	1
Raw Clay		5

DIFFERENT METHODS OF BLEACHING

According to Stern (45), soybean oil containing high concentration of pigment is first treated with charcoal and then with clay. This method is not applicable to oils which have already been treated with acid clay. A brief discription of this method is presented below:

Ten kg. of a dark green oil was pretreated with 100 gm. vegetable charcoal and then heated for 10 minutes at 85 C . The oil was then filtered off, diluted with 10 ml. hexane and treated simultaneously with 450 gm. sucrose plus 50 gm. clay. According to Stern (45), the results obtained were much better than the case when the clay was the only bleaching agent. In the present investigation , the above procedure is used, but the amounts are altered as follows:

Ten ml. of pirina oil , 1 gm. coconut charcoal, 10 ml. hexane , 0.45 gm. granulated sucrose and 1 gm. clay are used.

The experiment is performed on clays C_1 and C_2 . The results are presented in Table 34.

Table 34

$\lambda = 580\ m\mu$

Type of Clay	% Transmission R.A.B.	% Transmission 2 M.A.B.
C_1 - 31% HCl	60	65
C_1 - 40% HCl	70	82
C_2 - 30% HCl	45	51

CHEMICAL ANALYSES OF CLAYS

Table 35

Analysis of C_1 (Raw)

SiO_2	62.9%
Al_2O_3	15.3%
Fe_2O_3	3.8%
MgO	0.2%
CaO	0.6%
Loss on Ignition	7.1%
H_2O loss (105°C)	10.0%
Alkalies and Remainder	0.1%

Table 36

Analysis of C_1 (36% HCl pH 6)

SiO_2	65.9%
Al_2O_3	14.7%
Fe_2O_3	3.1%
MgO	0.2%
CaO	0.6%
Loss on Ignition	5.3%
H_2O loss (105°C)	10.0%
Alkalies and Remainder	0.2%

Table 37

Analysis of C_2 (Raw)

SiO_2	49%
Al_2O_3	11.2%
Fe_2O_3	4.3%
MgO	0.8%
CaO	0.0%
Loss on Ignition	22.0%
H_2O loss (105°C)	12.0%
Alkalies and Remainder	0.7%

X-RAY EXPERIMENTS

In the X-ray experiments copper tube is used and the resulting X-ray is K_{α}. Its wavelength is 1.54054 angstrom. The procedure followed to identify the crystal structure of C_1 , C_2 , C_3 and C_4 is described below :

The clays are powdered to 0.25 mm. size and then dried at 100°C for one hour. Samples are prepared in the form of squares as reported by Aytekin and Tulgar(53) . Their diffraction patterns are obtained at the Tecnical University of İstanbul. The diffraction patterns are presented in Figures 7,8,9,10 and 11.

Identification is done according to ASTM rules. Therefore identifications are done according to the following procedure :

most intense peak	100
intense peak	90-70
medium peak	70-50
least intense peak	50-10

In the patterns the highest peak is considered 100 % intense. The others are given intensity values in the relative manner. Obtaining the 2 θ values from the diffraction patterns, the d values are obtained from the formula:

$$n\lambda = 2\ d \sin\theta \qquad \text{where} \quad \lambda = 1.54054\ \text{Å}$$

After obtaining the d values and the corresponding intensities I , Numerical Hanawalt index is used. First d_1 value is determined, then the closest d_2 and d_3 values are found and hence the material which corresponds to the previously determined d_1 , d_2, and d_3 values. With the d_1 , d_2 and d_3 values , a corresponding ASTM card is chosen and the d values of the unknown are compared with the d values appearing in the ASTM card. When there is a complete correspondance between the two sets, the unknown is identified. The d, 2θ and I values of the clays C_1, C_2 , C_3, and C_4 are as follows :

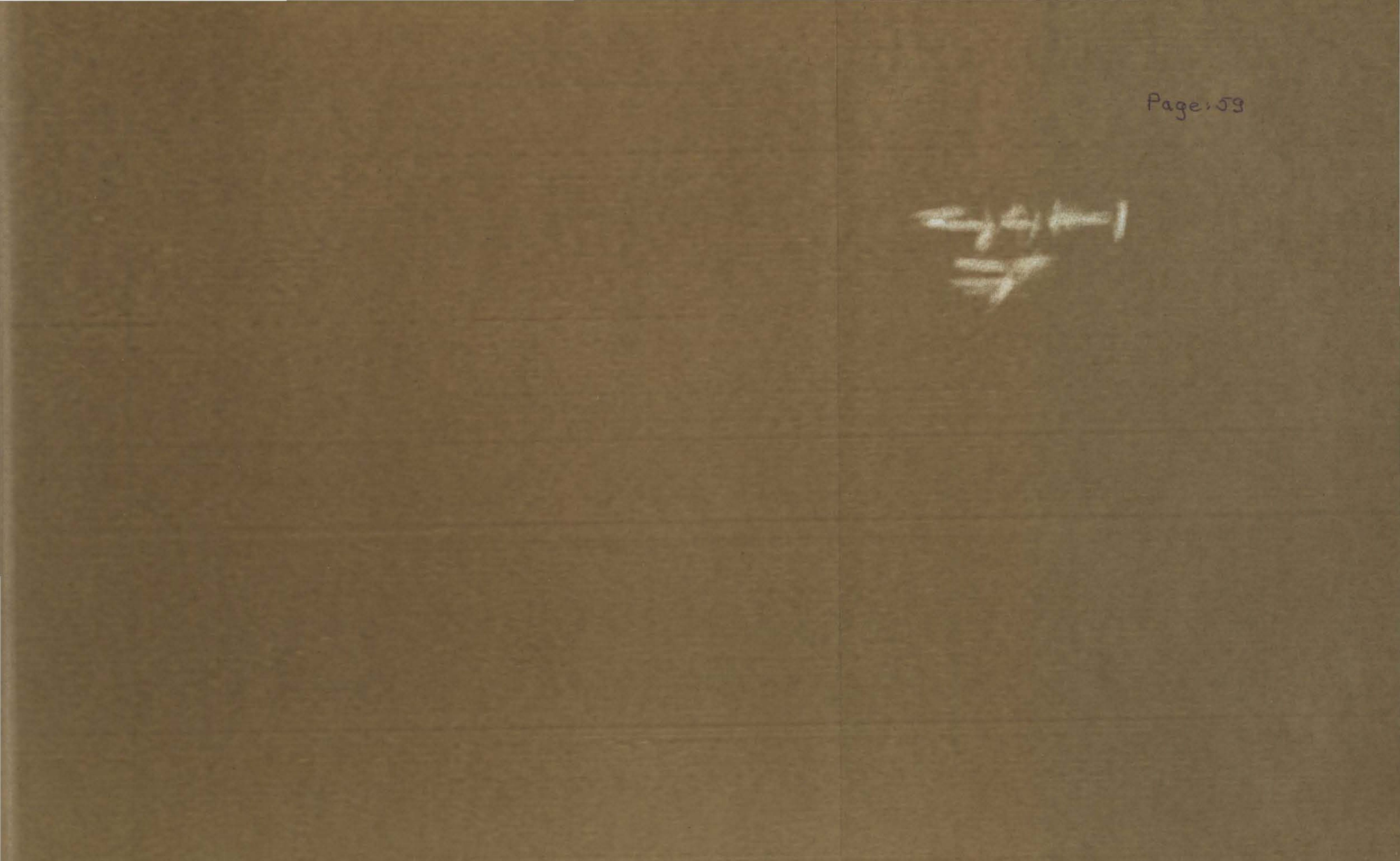


Fig. 7. Diffraction Pattern of Clay C_1 (Raw)

Table 38

C_1 (Raw)

2θ (°)	d (A°)	Peak Height (cm)	I
8.2	10.773	8.1	54
8.4	10.517	7	46.6
19.8	4.4800	8.5	56.6
20.8	4.2669	7.4	50
22.0	4.0368	6.5	43.5
23.6	3.7666	6.0	40.0
26.6	3.3482	15.0	100
27.4	3.2522	7	46.6
27.9	3.1951	8.8	59
34.4	2.6048	6.5	43.5

Fig. 8. Diffraction Pattern of Clay C_1 (activated with 35% H_2SO_4)

Table 39

C_1 35% H_2SO_4 (3 hr. activation)

2θ (°)	d (Å)	Peak Height (cm)	I
8.4	10.517	7	48.3
19.8	4.4800	8.5	58.5
20.9	4.2467	8	55
23.5	3.7824	5	34.5
25.4	3.5036	6	41.5
26.65	3.3408	14.5	100
28.1	3.1728	7	48.3
34.6	2.5902	6	41.5
35.1	2.5544	6	41.5

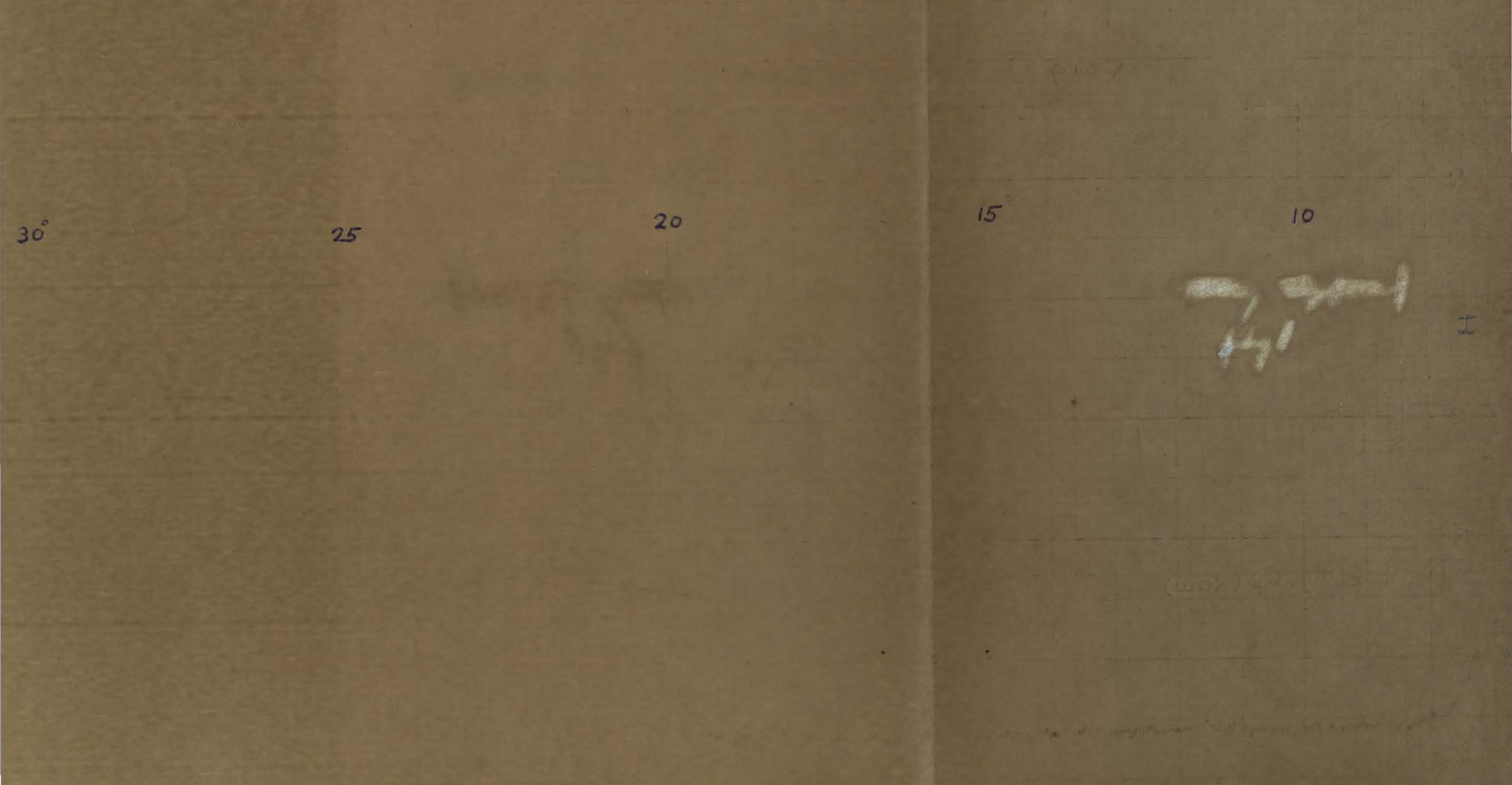


Fig. 9. Diffraction Pattern of Clay C_2 (Raw)

Table 40

C_2 Clay (Raw)

2θ (°)	d (A°)	Peak Height (cm)	I
7	12.617	13	94
15.9	5.5691	9.2	66
19.9	4.4578	8	57
20.0	4.4357	8	57
21.5	4.1295	6	43
23.7	3.7509	6.3	45
26.1	3.4118	14.0	100
26.8	3.3237	6.2	43
30.7	2.9097	10.2	73
35.3	2.5404	7	50

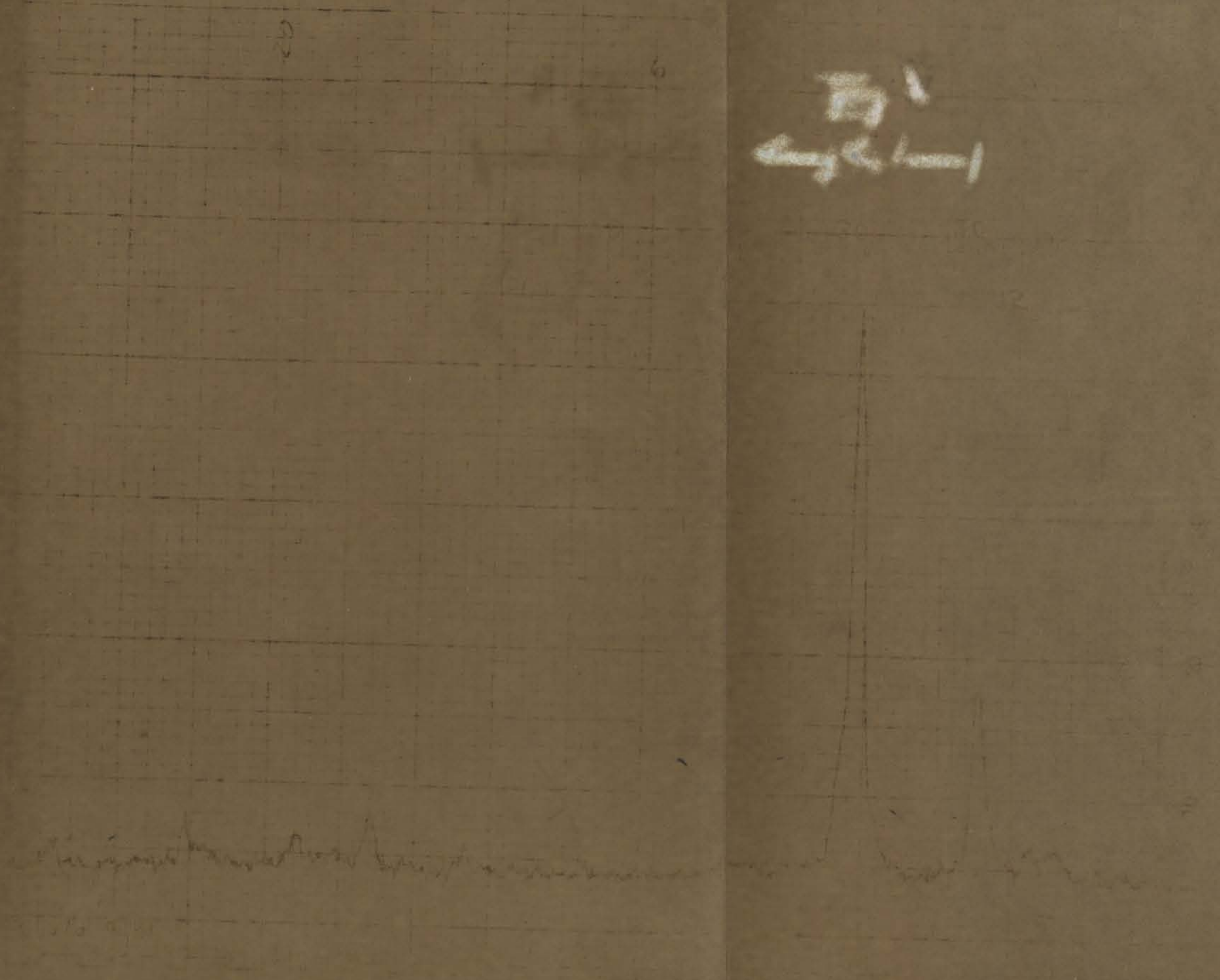


Fig. 10. Diffraction Pattern of Clay C_4 (Raw)

Table 41

C_4 (Raw)

$2\theta(^\circ)$	d (A°)	Peak Height (cm)	I
8.1	10.906	7	35
19.9	4.4578	7.1	35.5
20.9	4.2467	8.1	40.5
26.7	3.3359	20	100
31.0	2.8823	18.4	92
33.5	2.6727	5.5	27.5
35.4	2.5334	5.5	27.5
41.2	2.1892	8.1	40.5
45.0	2.0128	5.5	27.5

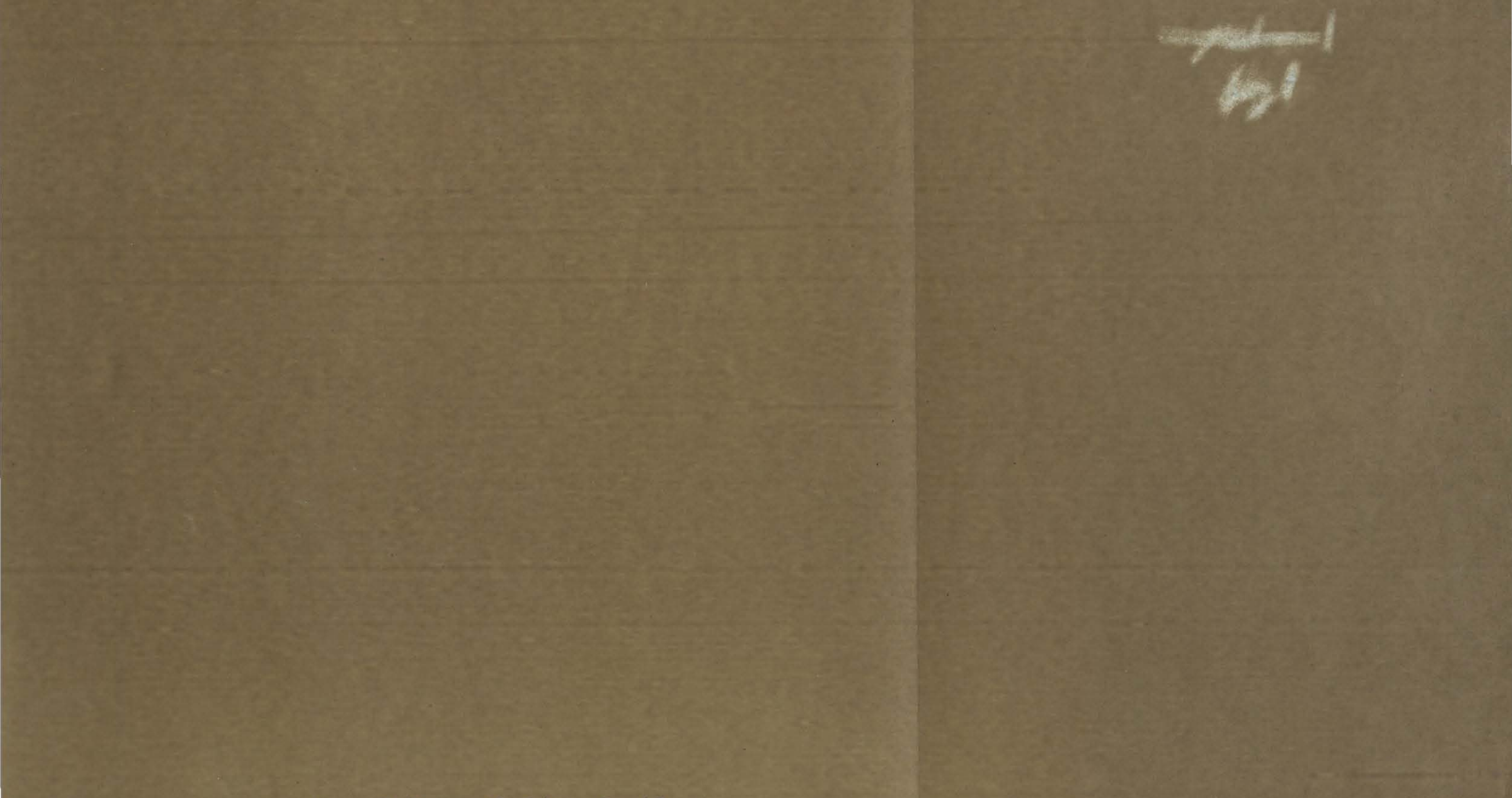


Fig. 11. Diffraction Pattern of Clay C_5 (Raw)

Table 42

C_5 (Raw)

2θ (°)	d (A°)	Peak Height (cm)	I
9.4	9.400	6.5	14.6
9.7	9.1103	6.7	15
10.5	8.4179	18.0	40
21.1	7.3081	44.8	100
17.3	5.1214	6	13.4
18.6	4.7663	8	17.8
21.1	4.2069	7.8	17.4
24.5	3.6302	24	54
22.8	3.8969	5.6	12.6
27.1	3.2875	8.1	18
19.6	4.5253	6.5	14.6
28.4	3.1399	26.8	60
30.4	2.9373	6	13.4
31.8	2.8115	6.2	13.8
33.0	2.7120	8	17.8
34.5	2.5974	5.5	12.3
35.5	2.5265	8	17.8
38.4	2.3421	6	13.4
41.7	2.1641	6	13.4

C_1 pattern is compared with the d values appearing on the ASTM card. Since all the d values agree, one of the components of the clay C_1 is Halloysite hydrated (endellite). $Al\ Si_2O_5\ (OH)_4 \cdot 2H_2O$.

Now we have to identify the other components of the clay C_1. The remaining d values of the diffraction pattern are considered. First, the following are chosen as d_1, d_2 and d_3 values.

$d_1 = 3.1951$

$d_2 = 4.4800$

$d_3 = 3.2522$

but no corresponding d_1, d_2, d_3 values are found in the Hannawalt index (32). Then:

$d_1 = 3.19$

$d_2 = 4.26$

$d_3 = 4.03$

still no corresponding values are found. Finally:

$d_1 = 3.1951$

$d_2 = 4.0368$

$d_3 = 3.2522$

are taken and the corresponding d_1, d_2, d_3 values appearing in the Hannawalt index are:

$d_1 = 3.180$

$d_2 = 4.03$

$d_3 = 3.20$

Corresponding to these d values ASTM card is 9 - 457. It is taken out. All the remaining d values of the pattern are compared since all the d values are in agreement. The second component of the C_1 clay is identified as OLIGOCLASE $0.83\ Na\ Al\ Si_3O_8\ 0.16\ Ca\ Al_2\ Si_2\ O_8$. Sodium calcium Aluminum silicate.

Similarly the other clays are identified. The results are:

C_2 clay is composed of:

Silver aluminum silicate hydrate $AgAlSi_2O_6 \cdot H_2O$ and of loughlinite ($Na_2\ Mg_3\ Si_6\ O_{16} \cdot 8H_2O$) corresponding ASTM cards are 2- 0420 and 13 - 310 respectively.

C_4 clay

Milarite $K\ Ca_2(Be_2\ ASi_{12})\ O_{30} \cdot 1/2\ H_2O$ and $Ca\ Rh_2$. The corresponding ASTM cards are 12 - 450 and 11 - 489 respectively.

C_5 clay

Gismondite ($Ca\ Al_2\ Si_2\ O_8 \cdot 4H_2O$) and $K\ Al\ Si\ O_4$. The corresponding ASTM cards are 2 - 0096 and 10 -466 respectively.

IV

RESULTS AND CONCLUSION

Examination of Figures 12 and 13 reveals that the proper amount of hydrochloric acid necassary to activate clay C_1 is 37 per cent. After two months of waiting time , transmission in all of the samples increased, i.e. for C_1 increase is from 82 to 94 per cent transmission. This increase is due to the fact that non-centrifugable clay particles have settled down during the period of waiting hence permitting a higher transmission of light. Still judging from the same graph , one sees that for clay C_2 curve there is a gap between the acid concentrations 30 and 40 per cent. This is due to the fact that experiments were not performed for the acid concentrations in between these values. However, the shape of the curve for C_2 indicates that there will be a peak similar to the curve for clay C_1. Hence C_2 might show high activity somewhere around these acid values.

Clay C_3 is somewhat activable clay eventhough it does not show much activity in this investigation. Its best activated state occured with 40 per cent hydrocholoric acid when it yielded 50 per cent transmission. This value is far from being satisfactory. Clays C_4 and C_5 showed no reaction to acid concentrations and even at high concentrations of acid their natural adsorbent power decreased. This might be due to collapse of structure. In examining Tables 29-33, it is clearly seen that the values obtained with spectrophotometer quite agree with the values found using methylene blue solution as the material to be bleached. With the 37 per cent hydrocholoric acid C_1, the result obtained still corresponds to the clay with the most powerful adsorbing capacity.

As the bleaching time is increased, the degree of decolorization increases. In the investigation only two samples, namely one at t = 25 minutes , the other at t = 40 minutes are taken. The 40-minute samples gave higher transmission values. However, this does not mean that bleaching or the decolorization continues indefinitely. The process of adsorption of coloring matters is of a reversible nature. After a given time the process of adsorption reverses itself and one gets desorption which is the undesired case.

The time of activation, when HCl is the activating acid, is three hours. However when H_2SO_4 is used, the activation period is six hours. Activation experiments of three-hour period for H_2SO_4 did not give satisfactory results.

The first bleaching method as indicated in Section III proved satisfactory. The second method is of no practical importance. Hexane method also gave satisfactory results, however it is inconvenient in the sense that its procedure is complicated, takes longer time and many reagents are required. However, hexane method is not tried for all clay samples. Therefore a completely conclusive statement regarding its efficiency cannot be made.

The results of the chemical analyses of the clays confirmed the hypothesis that acid activation increases the ratio of $SiO_2:Al_2O_3$. For C_1 clay this ratio is increased from ~~41~~ 4.1 to ~~45~~ 4.5. In addition there is an increase in SiO_2 percentage of the sample.

X-ray diffraction patterns are the most useful tools for the present investigation.

The most activable clay C_1 proved to consist of halloysite, which is the second critical material (after the montmorillonite) to give adsorbing capacity to the clays.

The X-ray diffraction patterns of C_1 before and after the activation process are exactly the same as shown in Figures 7 and 8. This indicates that the crystal structure of the clay is not destroyed during the process of activation as is asserted by Nagornaya (11). It is not true that only relics of the original mineral remain together with silica gel. But destruction of crystal structure might occur only with montmorillonite (12). Further experiments should be done along this line.

The efficiency of clay materials for adsorption is also a function of drying temperature. Although C_1 clay activated with 37% HCl gave good results, when this clay was air dried the transmission obtained at 530 mμ was only 30%.

Burghardt (5) in one of the steps in activation procedure allows live steam at two or three atmospheres through an acid proof distributor and brings the system of clay and acid to boiling. Also pure wood vessel and agitator are used as reaction vessel.

In this work, glass apparatus was used and boiling was conducted at one atmosphere pressure without using live steam. This proves the fact that pressure increase and the quality of apparatus have no effect on the activation. However it is confirmed that use of the nitrogen instead of air and use of increased pressure have considerable effect on bleaching capacity.

The hypothesis advocated by Ichiro-Harada (36) that carotenoids and xanthophylls absorb light of 400 - 90 mμ while chlorophyls absorb at 670 - 80 mμ could not be fully studied. If one refers to figure 14, it is seen that at 670 - 80 mμ and 400 - 90 mμ transmission values are small therefore bleached oil readings were taken at 530 mμ where the transmisson was the highest. Accordingly nothing can be stated regarding the removal or presence of chlorophyls, xanthophylls and carotenoids from the bleached oil.

The activation mechanism in literature mostly related to montmorillonite (14), (15), (24), (22) and the changes due to the changes in its crystal lattice. However none of the clays investigated in this work contained montmorillonite mineral. As it is determined using X-ray diffraction patterns in section of experiments, C_1 clay is composed of halloysite and of oligoclase (sodium calcium aluminum silicate). Clay C_2 is composed of silver aluminum silicate hydrated and of lonchlinite. Clay C_1 is composed of milarite and of $CaRh_2$ and clay C_5 is composed of gismondite and of K Al Si O_4. (refer to figures 7 through 11) Therefore activibality and high adsorption power is not only due to montmorillonite mineral and its crystal change. It might be due to the orientation of the polar groups or organic acid molecules toward the surface (15) of the adsorbent or it might be due to the electric charge of the crystal lattice as it is asserted by Sh. Battalova (14). Excess electric charge attracting the polar groups or organic acids present in the oil is confirmed with the present investigation since halloysite crystal lattice is not effected by acid treatment, bleaching capacity of it might be due to result of electric attraction resulting between halloysite and polar groups in the pirina oil.

The clays under investigation were not controlled for sulfur content. Whereas to clays containing sulfur not in the form of sulfates, a different procedure should be applied as is explained by Eberhard Leiste (44). Because sulfur remains in the activated product and partly passes from there into the bleached product the same restriction holds if the activation is carried out with acids containing sulfur or steam-distillable organic impurities. Some of the clay samples in fact were treated with H_2SO_4 but the very last restriction does not apply to our case since all the acids used in the experiment were pure HCl and H_2SO_4, free from organic impurities. However, the clays used might contain S in the form of pyrites. This fact was overlooked in the experiments and its effect on the bleached oil was not determined.

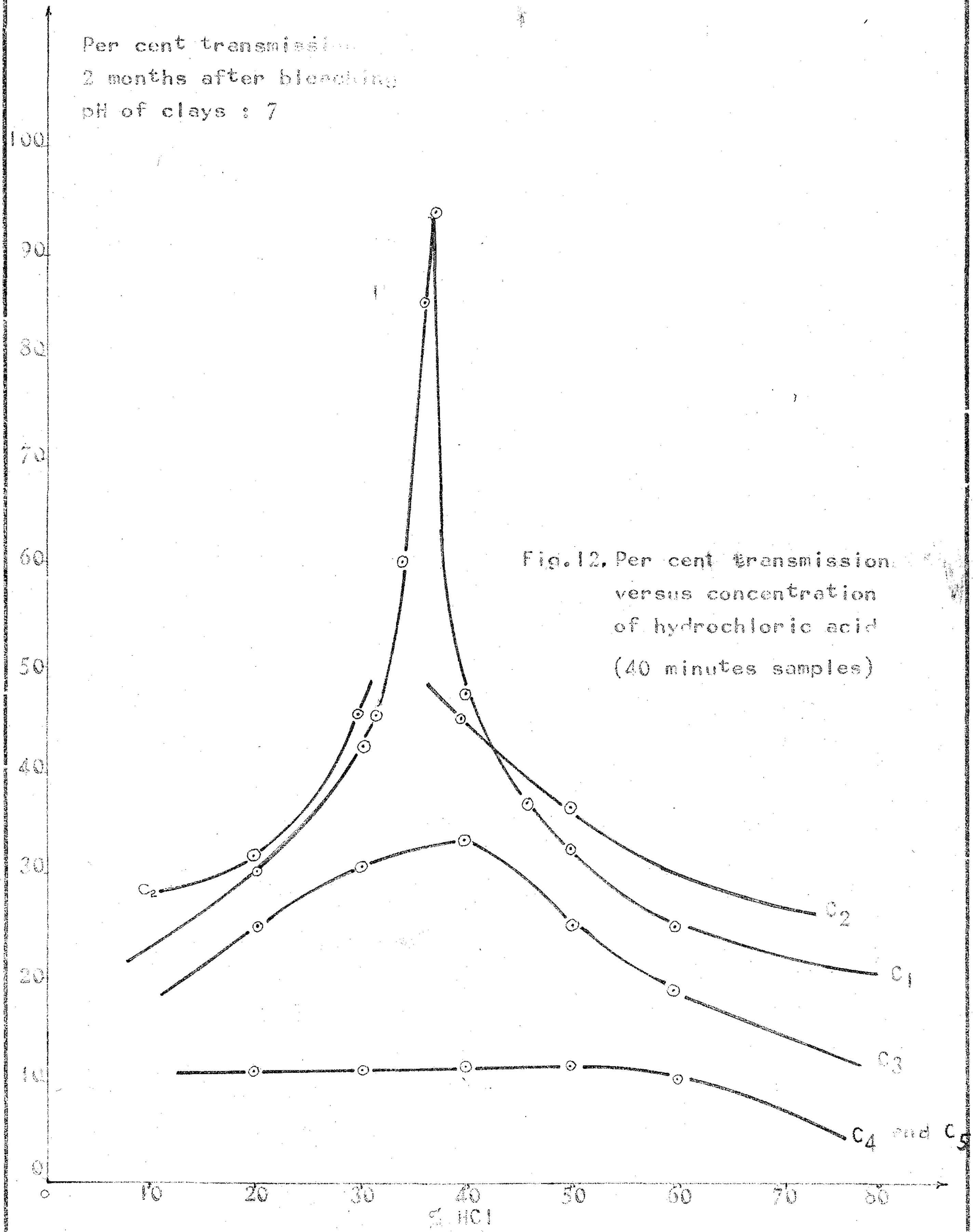


Fig. 12. Per cent transmission versus concentration of hydrochloric acid (40 minutes samples)

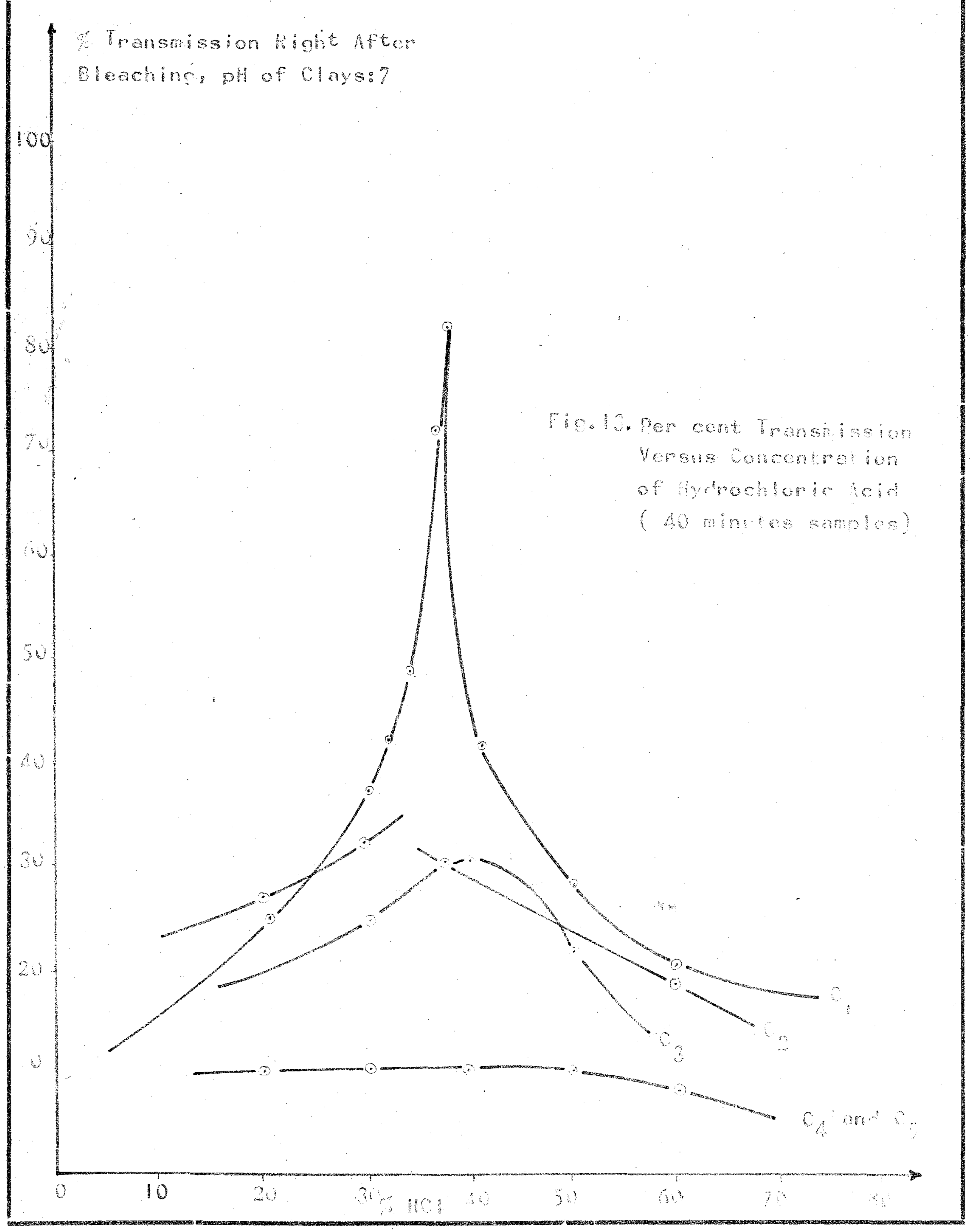


Fig. 13. Per cent Transmission Versus Concentration of Hydrochloric Acid (40 minutes samples)

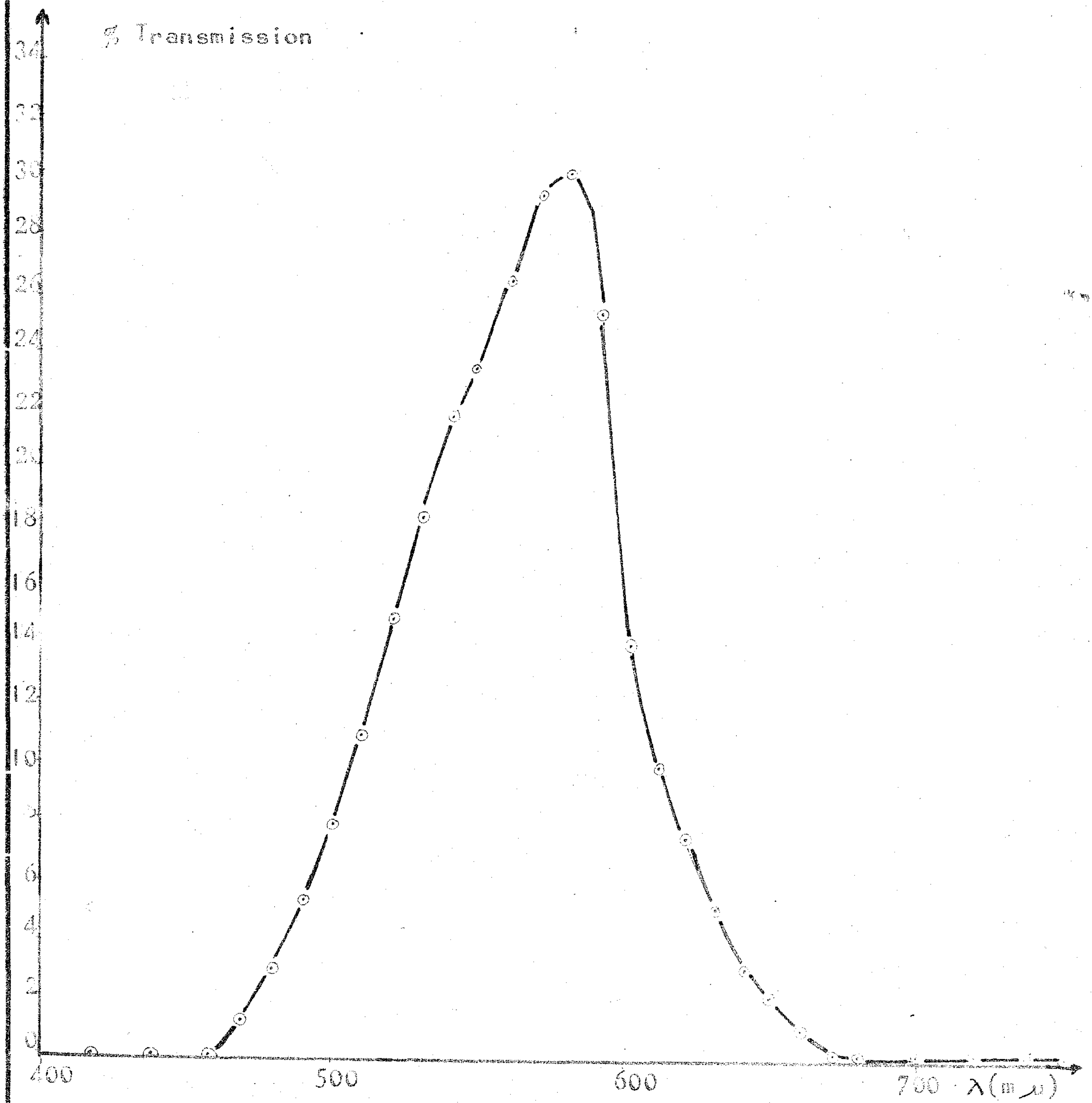


Fig. 14. Per cent transmission versus wavelength

V

SUGGESTIONS FOR FUTURE WORK

1- A geological consideration shows that Turkey possesses a large deposit of activable clays. Therefore, more samples of Turkish clays can be worked on to increase their adsorptive powers.

2- During the experiments not all of the activation variables were considered. Mainly seven were varied, the remaining three being kept constant. If these three variables are also considered in future experiments, the phenomena of bleaching and activation can be more clarified. According to the author's investigations only two people in Turkey namely, Saim Aktürk, a chemical engineer, from Maden Tetkik Arama Enstitüsü and Hüseyin Bentürk, the head of Teknolojik Araştırmalar Merkezi, made studies on the refinement of oils by bleaching earth.

3- As is apparent from the previous considerations, no sound theory of activation and bleaching is available. Experiments utilizing X-ray diffraction patterns together with electron microscope can be done to determine mechanism of activation.

VI

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