ACTIVATION AND CLARIFYING PROPERTIES OF FULLER'S EARTH.

PART III. BLEACHING OF SAFFLOWER OIL BY FULLER'S EARTHS.

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Inferring from the results given in Part II (This *Journal*, 1937, 20A, 111) we concluded that the reactivity of the earth in the bleaching and clarifying processes is due to the zeolitic hydrogen present in the earth. This idea is supported by the fact that large quantities of hydrochloric acid are required for activating fuller's earth, that such earths liberate acid when treated with salt solutions and that the acid liberated is proportional to the amount of colouring matter romoved from a sample of groundnut oil.

In this paper we have presented the results obtained in the decolorisation of safflower oil by the various earths used in Part II, and also when these were treated with different salt solutions so as to convert the hydrogen zeolite into sodium, potassium, calcium, magnesium and aluminium zeolites. The latter were found to be comparatively poor in bleaching property.

Acting on our postulate that the activation of fuller's earth is due to the formation of hydrogen zeolite in the body of the earth, we studied the effect of electrodialysis and electrolysis on the fuller's earth. From the results so far obtained, it has been noticed that the fuller's earth is activated when subjected to such treatment and that the sodium and other bases contained in the original earth are removed and substituted by hydrogen. This method may obviate the very expensive method of activation by hydrochloric acid.

EXPERIMENTAL.

The procedure followed was the same as that adopted in Part II. In order to increase the accuracy of measurement, a sample of safflower oil manufactured in Bijapur by the country process and having an acid value 0.08 and colour 12.7 (yellow) and 0.8 (red) in Lovibond units, was used for the decolorisation of experiments. The pH measurements recorded refer to a mixture 2 grams of earths with 100 c.c. of normal sodium chloride solution, unless otherwise stated.

The following results were obtained with the original earths as such and when they were washed free from alkalies and soluble salts. The latter process resulted in a loss of the finer particles which were brought in suspension.

	Original Earths			Washed Earths		
	Change in Lovibond unit	pH	pH × change	Change in Lovibond	pH	pH × change
Kolhapur	7·9	7·0	55	8·7	6·8	59
Jodhpur	8·5	7·65	57	10·4	6·0	62
Bhawanagar	6·7	8·51	57	7·4	8·3	61
Murwara, C.P.	8·0	7·40	59	8·2	7·0	57
Katni	8·2	6·63	54	8·5	6·6	56
Florida	11·8	3·08	36	..	..	..
Germany	11·8	3·02	36	..	..	..

The average values of the product of pH and change in Lovibond units (yellow) are, 56.5 in the case of original earths, 59 in the case of washed earths and 36 in the case of foreign earths which are obviously activated products as shown in Part II. The washing slightly improved the bleaching power of the earths and there was also a corresponding decrease in the pH.

Experiments were next conducted with activated earths. The results are given in the following table.

Activated Earths.

	Lovibond in Change	pH	pH × change
Kolhapur	10·2	3·20	33
Jodhpur	11·7	2·92	34
Bhawanagar	9·5	3·64	35
Murwara, C.P.	9·2	3·70	34
Katni	9·5	3·58	34

The product of pH × Lovibond is 34 as compared to 36 obtained with foreign earths. These results conclusively prove the role of hydrogen zeolite in the fuller's earth in decolorisation.

Displacement of Hydrogen by other bases.—To study the displacement of hydrogen by different bases, the activated Jodhpur earth was shaken with normal solutions of KCl, $CaCl_2$, $MgCl_2$ and $AlCl_3$, and the pH of the resultant mixture was measured. The following results were obtained:

N solution	pH
KCl	2.86
NaCl	2.92
$CaCl_2$	3.24
$MgCl_2$	3.30
$AlCl_3$	3.30

A quantity of the earth was also boiled with concentrated solutions of these salts and washed completely and the bleaching values and pH against normal solutions were measured. The following table gives the results:

Jodhpur Activated Earth.

Solutions	pH	Change in Lovibond
KCl	4·32	9·1
NaCl	4·21	9·1
$CaCl_2$	3·72	8·8
$MgCl_2$	3·48	8·9
$AlCl_3$	3·60	8·9
KOH	6·42	7·2
NaOH	6·39	7·3

On boiling the earth with the concentrated salt solutions, a portion of the hydrogen is lost and is replaced by the corresponding base. The results show that hydrogen can be displaced by other bases, thus proving the zeolitic nature of the hydrogen. The maximum displacement is effected by potassium, magnesium and aluminium having the least effect. The earths with the new base show deterioration in the bleaching power as is seen from the last column. On the basis of the theory of calcium zeolites as being responsible for action of fuller's earth (Fogle and Olin, *Ind. Eng. Chem.*, 1933, 25, 1069), earths treated with calcium and magnesium salts ought to have shown 100 times, and those treated with aluminium salts many more times the activity of the earths treated with monovalent salts. The results show that such is not the case.

The hydrogen gets completely displaced on treatment with alkalies, and the earth degrades in quality to the level of that of the original earth.

Electrodialysed and Electrolysed Earths.—If the activity of the earth can be improved by displacement of other bases by hydrogen, such a displacement could be brought about by electrodialysis of the earth and their activity improved. With that view the Jodhpur and Bhawanagar earths were subjected to electrodialysis in a three compartment cell. A suspension of the earth which was constantly stirred, was contained in the middle compartment separated from the adjoining compartments by porous plates. The other two compartments through which distilled water was circulated, held a platinum anode in one and a nickel cathode in the other close to the porous walls. A potential of 200 volts was applied. In the case of the original earths, the water-level in the central compartment gradually decreased in the initial stages and became stationary for a short time and rose again. Electro-dialysis could not therefore be continued as water-level rose in the central compartment due to electro-capillary effect. In the case of the activated earth no initial decrease was observed.

It was therefore decided to electrolyse the suspension by placing the anode in the central compartment. In this case the water migrated from the central compartment to the cathode compartment and was constantly replenished. The current strength which was about 0.7 amp. in the beginning gradually decreased to less than 0.05 amp. after electrolysis for about 48 hours. The bases extracted were mainly sodium and calcium ions in the form of hydroxides. When the current strength decreased to about 0.05 amps., the earth was taken out, washed and dried, and its bleaching value and pH were tested.

In the case of the original earth the process was fast in the initial stages, the suspension being highly conducting due to dissolved bases, thus increasing the activity of the process.

The following table shows the results:—

Earth	Change in Lovibond	pH	Earth	Change in Lovibond	pH
Jodhpur earth			*Bhawanagar earth*		
Original	8·5	6·65	Original	6·7	8·51
Electrolysed	10·6	3·57	Electrolysed	7·0	8·17
Activated	11·7	2·92	Activated	9·5	3·64
Electrolysed	11·7	2·90	Electrolysed	9·7	3·54

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The results show that the activity of the earth can be increased by subjecting the earth to the electrolysis in the manner described. The increase is very marked in case of Jodhpur earth which, on electrolysis, shows nearly as much activity as the acid-treated earth. Bhawanagar earth shows similar increase though not to the same extent. The activity of the acid treated earths remains unaffected by electrolysis.

SUMMARY.

Further evidence has been brought forward in support of the hydrogen zeolite theory of decolorisation of oils by fuller's earth using safflower oil and earths treated in different ways.

Calcium and aluminium earths were inferior in bleaching action. Activated earths are deactivated when treated with alkalies.

It has been shown that one of the Indian fuller's earths could be activated by subjecting its suspension to electrolysis.

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