

ACTIVATION AND CLARIFYING PROPERTIES OF FULLER'S EARTH

PART VII. ACTIVATION OF FULLER'S EARTH.

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In previous parts¹ the fuller's earths from different sources in India as well as from foreign countries were tested for their decolorising properties. It was found that the *pH* of the extract, obtained by shaking a quantity of the earth with sodium chloride solution, showed close relationship with the decolorising power of the earth: the higher the decolorising power, the lower the *pH* of the extract. This relationship held in the case of all samples of the earth whether raw, acid activated, electrolysed and electro dialysed or dehydrated to different extents. The inverse proportionality between the bleaching value and the *pH* was seen from the constancy of the proportionality factor (*pH* × decolorising power). The relationship also held in the decolorisation of two different vegetable oils.

The observed relationship between the *pH* and the activity of the earth is to be explained by the fact that the *pH* of the extract is a measure of the exchangeable hydrogen content of the earth and it is this hydrogen content which appears to be responsible for the activity of the earth.

In a study of the removal of colouring matter by fuller's earth from a vegetable oil, it was found that the colour was not totally removed by physical adsorption, since the various requirements of the Freundlich isotherm could not be fulfilled. The nature of the decolorisation curves showed that only a small proportion of the colouring matter was removed by adsorption and the rest by chemical reaction with the active element in the earth. With fine-grained earth, decolorisation could be expressed by a modification of the Freundlich equation $x/m = ac^n + bc$, where *bc* accounts for the chemical effect. Taking into consideration the existence of base-exchange reactions usually found in clay materials and the observed relationship between the *pH* and the decolorising power of the earth, the chemical reactivity of the exchangeable or zeolitic hydrogen in the earth with the colouring matter of the oil became obvious.

When hydrogen earths were converted into sodium, magnesium, calcium or aluminium earths by treatment with the corresponding salts, the activity of the earth was considerably reduced. The activity could, however, be restored by treating these earths with a small quantity of hydrochloric acid. The replacement of the bases by hydrogen could also be effected by subjecting the earth suspension to electrolysis or electro dialysis, when calcium, sodium

and aluminium could be found extracted in the wash and the decolorising power of the earth increased. The electrolytic activation of the earth could be augmented by addition of small quantities of acid which helped towards further extraction of the bases. The activity of the earth was found to have no relation with the exchangeable calcium as postulated by Folge and Olin² or with the combined action of exchangeable aluminium and hydrogen as suggested by Hofmann and co-workers.³

The activity of the earth was, however, found to depend on the nature of the essential mineralogical constituent of the earth as found by Hofmann. From the nature of the dehydration curves and their comparison with those of well-known clay minerals, the earths could be classified with regard to their mineralogical origin. Active earth showed high proportion of montmorillonite, while in the less active ones kaolinite predominated. The higher activity of the montmorillonite earth is in agreement with the fact that montmorillonite is characterised by a high zeolitic exchange. From the rate of dehydration and the amount of water loss, the two types of water, namely, adsorbed water ('planar' and 'broken-bond' water) and the crystal lattice water derived from the H and OH planes, could be distinguished. A study of the activities of the earth samples dehydrated to different extents showed that while the loss of the planar water increased the activity of the earth, the loss of crystal lattice water affected the activity adversely.

These results gave an insight into the mechanism of the activation of the earth by the various processes studied.

In activation of the earth by electrolysis and electro dialysis the hydrogen derived from water replaces the various bases which are extracted at the cathode in the form of hydroxides.

In activation by acids, the action of acid results in reducing the earth to the fundamental montmorillonite structures, replacing the bases by hydrogen and opening the crystal channels by dissolving the adhering impurities. This facilitates zeolitic exchange of hydrogen when treated with salt solutions.

In acid activation the nature of the anion in the acid employed has thus no influence. The difference in activation, brought about by hydrochloric acid on one hand and sulphuric acid on the other, is due to the insolubility of calcium sulphate, the deposition of which clogs the crystal channel and thus lessens the exchange capacity of the earth.

That an activated earth behaves as a hydrogen zeolite is further shown by the fact that the hydrogen can be progressively replaced by using higher and higher concentrations of a replacing cation. Accurate measurements by conductivity method of the hydrogen ion so extracted showed that the replacement proceeds according to the law of mass action:

$$K = \frac{[H^+]^2}{[\square-H^+ - H^+][Na^+ - H^+]}$$

where $\square-H$ denotes the earth complex.

The low value of the equilibrium (K) found indicated that the hydrogen is tenaciously held to the surface. This observation is in conformity with the peculiar behaviour of hydrogen in hydrogen clays found by Weigner and Jenny.⁴

It has long been advocated by Eckart⁵ and also by Weldes⁶ that the increased activity of the earth on acid treatment is due to the dissolution of alumina and silica from the body of the earth resulting in an increased porosity and absorption. The increased porosity cannot, however, explain the direct dependence of activity exclusively on the hydrogen zeolitic content of the earth. In the light of the above results the increased activity is to be attributed to the removal of most of the extraneous matter from the earth and to the opening of the crystal channels, making the exchangeable hydrogen available for reaction. Prolonged digestion with acid impairs the activity because it results in the decomposition of the montmorillonite structures. The results obtained in the present paper are in support of this view.

For the manufacture of activated fuller's earth, the following processes have been tried: (1) simple roasting (calcining); (2) digestion in acid solutions, or in mixture of acid solutions and salts; (3) digestion in alkalies; (4) subjecting the dry earths to gaseous acids; and (5) electrolysis and electro dialysis of aqueous suspensions. The suitability of any of the above processes for adoption on a commercial basis is governed by the nature of the raw material. So far as most of the common earths and, particularly, Indian earths are concerned, the processes 1, 4 and 5 are unsuitable, as, either they yield unactivated or only weakly activated products or the cost of their operation is forbidding. In acid activation, nitric, oxalic and sulphurous acids are unsuitable. For Indian earths, only sulphuric and hydrochloric acid solutions have been found to give promising results as the activating agents. The optimum conditions of operation with regard to each of the two reagents have been determined in the present investigation.

Although deposits of fuller's earth are spread all over India, a commercially workable supply is obtainable only at a few deposits. The following table shows the output of fuller's earth in India from 1933 to 1937:—

	1933	1934	1935	1936	1937
	Tons.	Tons.	Tons.	Tons.	Tons.
Hyderabad (Sind)	.. 688	821	685	879	..
Khairpur State 3,776	4,281	4,201	2,928	4,844
Bikaner 1,491	2,213	1,437	1,514	869
Jaisalmer 17	18	17	17	13
Jodhpur 1,250	1,168	1,260	1,251	1,640

In the present research we have used the earth from Hyderabad (Sind).

EXPERIMENTAL.

(I) Activation with hydrochloric and sulphuric acid solutions: The method of activation consisted in heating under reflux a weighed quantity of earth

with a measured volume of acid solution of a known strength. After digestion for about three hours, the mixture was filtered through a buchner. The earth was washed free from acid dried at 110° before testing for activity. The volume of the acid solution used was such as to sufficiently cover the earth in the digestion flask. The proportion of the volume of the acid solution to the quantity of the earth was 200 c.c. of acid solution : 100 gms. of earth. The decolorising experiments were carried out on a sample of safflower oil, the original colour of which was 9.8 yellow Lovibond units, using 1% earth. The following table gives the results :—

Hydrochloric acid.

Acid strength.	Loss of earth in activation. %	Units of Lovibond colour removed.
1N	12.0	7.1
3N	20.1	7.5
5N	27.7	8.5
7N	32.4	4.4

Sulphuric acid.

Acid strength.	Loss of earth in activation. %	Units of Lovibond colour removed.
1N	11.5	6.9
3N	18.0	7.4
5N	23.5	8.4
7N	25.7	7.4

It will be seen that the activity of the earth obtained is highest at 5N acid strength, and drops below and above that strength. The earth, however, suffers progressive loss in weight with the acid strength indicating that with higher concentration of acid solutions more decomposition of the earth takes place with loss in activity.

The action of sulphuric acid is consistently of lower order than that of hydrochloric acid. Here also highest activity is obtained at 5N acid concentration.

(II) Activation with mixtures of sulphuric and hydrochloric acids was carried out and the activity of the product determined. The acids were mixed in equal proportions to give the suitable strengths. The following table gives the activity of the treated earths :—

Acid mixtures.

Total strength of the acids.	Units of Lovibond colour removed.
3N	7.5
5N	7.4
7N	6.2

The activity of the product is lower than that obtained with a single acid. Mixtures of acids in various other proportions were tried but all gave lower activity than the product obtained with 5N sulphuric acid.

(III) Activation of the earth was tried with sulphuric acid solution to which an equivalent amount of sodium chloride was added. The following results were obtained:—

Acid strength.	Lovibond units of colour removed.
3N	7.2
5N	7.4
7N	6.2

Here the activity obtained is almost the same as with the mixture of acids.

(IV) *Dry Process*.—In this method a thick paste was formed by grinding with the powdered earth a requisite volume of concentrated sulphuric acid. The paste was heated in a porcelain basin on a sandbath for about two hours at 150°C. The dry product in the basin was powdered and washed free from acid and dried. The following table gives the results:—

H ₂ SO ₄ per 100 gms. of earth.	Equivalent Normality in the wet method.	Loss of earth on activation. %	Unit of Lovibond colour removed.
10	1.02	7.5	7.2
20	2.04	10.6	8.4
30	3.06	12.4	8.3
40	4.08	15.6	7.0
50	5.10	17.7	5.4
60	6.12	20.5	3.9
70	7.14	21.4	2.3
80	8.16	22.6	1.8
90	9.18	23.7	1.6

There was no free acid in the filtrate. The results show that highest activity is obtained with 20 to 30% sulphuric acid. In the wet process this acid quantity would amount to 2.04N and 3.06N and gives a product the activity of which is as much as that obtained with 5N sulphuric acid solution in the wet process. If the activation is carried at about 200°C., the activity is found to decrease and the iron salts decompose into insoluble iron oxide which colours the final product.

It is intended to try this process on a semi-commercial stage.

SUMMARY.

A review of previous work of the authors on the activation and clarifying action of fuller's earth is given.

A dry process of activation which consists of heating a mixture of the raw earth with 20% of sulphuric acid at 150°C. gives a satisfactory product.

REFERENCES.

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- ⁴ Wiegner and Jenny (*Kolloid. Z.*, 1927, **42**, 268).
- ⁵ Eckart, *Die Bleicherde*, 1925.
- ⁶ Weldes (*L. Angew Chem.*, 1927, **40**, 79-82).