SUMMARY OF REPORT No. RD.68

"ACTIVATION OF CLAYS"

by

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1. INTRODUCTION.

Certain clays possess somewhat remarkable adsorptive properties, and their active nature has long been known and used in industry. The name "fuller's earth" given to these naturally active clays was derived from the early use in "fulling", the operation of removing grease from woollen goods.

Active clays are used in the refining of waxes, fats, vegetable and animal oils, and petroleum fractions. They are used as decolourizers, adsorbing coloured material from the crude stock to yield a clean light coloured product. In the United States the petroleum industry accounts for over 90 per cent of the annual domestic consumption.

Many different clays have proved useful as decolourizing agents, although quite often it is found that of two clays which appear structurally and chemically the same, one may be suitable for decolourizing oils while the other is of little use in this respect.

Clays of the montmorillonite group are usually associated with a high degree of activity. They possess relatively large numbers of exchangeable cations, and high exchange capacity has been associated with decolourizing ability. However, no general relationship has been found between exchange capacity and activity. Although active clays usually have relatively high capacities, not all clays of high capacity are active.

Some naturally active clays have been improved by acid leaching; in fact some of the best decolourizing clays are prepared from certain bentonites of relatively low natural decolourizing activity.

Clays from various localities in South Australia have been tested to determine the activity of both natural and acid treated material. The clays have been tested particularly for application to the decolourizing of reclaimed automotive lubricating oils.

Used lubricating oil may be reclaimed by heating with sulphuric acid (using superheated steam), neutralizing with calcium carbonate and filtering. The resulting oil still contains oxidation products in solution and is very dark coloured, in fact almost opaque. Treatment with active clay at elevated temperatures followed by filtration yields a light golden-brown oil of suitable quality for re-use as a lubricant.

2. MATERIAL EXAMINED.

The clay samples examined are listed below:

Sample		Predominant Mineral Component
C	Hallett's Cove, S.A.	Illite
D	Port Willunga, S.A.	Illite
F	Hackham, S.A.	Montmorillonite
O	North of Pt. Augusta, S.A.	Quartz, Montmorillonite
P	North of Pt. Augusta, S.A.	Quartz, Montmorillonite
Q	West of Pt. Augusta, S.A.	Quartz, Montmorillonite
S	North of Pt. Augusta, S.A.	Quartz
T	Echunga, S.A.	Montmorillonite
V	Ochre Point, S.A.	Kaolinite (white Ochre)
W	Ochre Point, S.A.	Kaolinite (red Ochre)

3. ANCILLARY MATERIALS.

A sample of used oil which had been reclaimed except for decolourizing was used to test all clays and acid-leached products. An imported fuller's earth was used as the basis of comparison. Normal laboratory reagents and equipment were used for leaching.

4. EXPERIMENTAL PROCEDURE AND RESULTS.

Elutriated samples of clays were used for leaching tests. A leaching procedure was adopted in which 15 g. (dry weight) of clay was heated at boiling point under reflux conditions with sulphuric acid of various concentrations at a pulp density of 30 per cent solids, for various periods of time.

The leached clays were filtered and washed with distilled water. The products were air-dried and ground to pass 200 mesh (BSS).

Natural clays and treated clays were tested for activity by the following method:

20 ml. of dirty oil in a 50 ml. beaker was mechanically stirred and heated on an electric hot-plate. When the oil temperature reached 40°C, 2 g. (dry weight) of clay was added and thoroughly mixed in. The mixture was heated at a rate which brought the temperature to 150°C. in ten minutes, and this temperature was maintained for a further ten minutes. The oil was then filtered through a close paper on a small Buchner funnel, and collected in a dry flask. The funnel was kept hot by means of an electrical heating tape during filtration. 10 ml. of the filtered oil was diluted to 50 ml. with light kerosene, and the optical transmission measured at a wavelength of 430 millimicrons. The standard for reference was the diluted oil obtained by treating dirty oil with the imported fuller's earth in a similar manner.

The activities of the various clays are expressed as percentages of the activity of the imported fuller's earth. Leaching conditions and activities of treated and untreated clays are shown in Table 1.

TABLE 1.

Acid Leaching of Clays.

	Acid Strength (% w/v)	Leaching Time (hr.)	Activity of Product (%)
Imported fuller's earth	-	-	100
Hallett's Cove, C.	-	-	50
" "	10	5½	70
" "	15	5½	75
" "	20	5½	82
" "	15	10	82
" "	20	10	79
" "	25	10	74
" "	20	8	78
Port Willunga, D.	-	-	56
" "	30	½	87
" "	30	1	93
" "	30	1½	99
" "	30	2	92
" "	30	4	90
" "	30	6	89
" "	20	1	81
" "	20	2	89
" "	20	4	94
" "	20	6	93
" "	20	8	86
" "	25	6	90
" "	10	6	87
Hackham, F.	-	-	41
" "	25	5½	97
" "	10	5½	68
" "	20	5½	92
" "	30	5½	99
" "	25	8	95
North of Pt. Augusta, O.	-	-	27
" " "	30	3	69
" " P.	-	-	27
" "	30	3	69
West of Pt. Augusta, Q.	-	-	29
" "	30	3	91
North of Pt. Augusta, S.	-	-	27
" "	30	3	33
Echunga, T.	-	-	53
"	30	3	89
"	30	6	87
"	30	2	83
"	30	1	81
"	20	8	79
"	20	4	79
"	20	2	78
Ochre Point, V.	-	-	12
" "	30	3	15
Ochre Point, W.	-	-	10
" "	30	3	15

5. DISCUSSION.

5.1 Leaching of Activable Clays: Effects of Acid Strength and Leaching Time -

The tests carried out on the activable clays C, D, F and T were not extensive, but were sufficient to indicate certain effects of leaching conditions.

The activity of a clay improves with leaching to a maximum value and further leaching causes a decline in activity.

To achieve maximum activity it appears that the amount of material leached from the clay has an optimum value. Mills et all (1950) have shown the connection between the amount of basic constituents removed and the activity of a clay. Further, they claimed that removal of the same amount of basic constituents from a clay yielded products of equivalent activity regardless of the leaching conditions employed. The connection between the amount of leaching and activity is borne out by the present data, and, in fact, analyses have shown that the amount of alumina leached from these clays is a critical factor. However, the other finding is not definitely supported in all instances. It appears that leaching with stronger acid for a shorter period may be more beneficial than leaching with weaker acid for a longer period. This is most apparent in the case of Echunga clay, T. Figure 1, shows typical graphs of activity plotted against leaching time for constant acid strengths of 20 per cent and 30 per cent respectively, from the data on Port Willunga clay, D. For constant acid strength, the leaching time is representative of the amount of basic constituents removed. The graphs show the decline in activity with over-leaching.

5.2 Individual Clays -

(i) Halletts Cove Clay, C.

This clay responds to acid treatment yielding a product of reasonably high activity which could possibly be suitable for industrial use. Acid required for treatment would probably be of the order of 650 lb. of sulphuric acid per short ton of raw clay.

(ii) Port Willunga Clay, D.

This clay yielded a product considerably more active than that from Hallett's Cove Clay, using a similar quantity of acid.

(iii) Hackham Clay, F.

This clay can be made almost as active as the imported fuller's earth. Acid required for treatment would probably amount to 850 lb. of sulphuric acid per short ton of raw clay.

(iv) Clays from beyond Pt. Augusta.

Clays, O, P, Q and S were from remote areas beyond Port Augusta, and the deposits would thus be of little interest. The samples were surface dusts, and all contained less than 50 per cent of clay fraction. Tests were carried out on elutriated fractions.

Samples O, P. and Q responded well to acid treatment, particularly Q, but none of these would be of commercial interest on account of geographical situation and the ill-defined nature of the deposits.

(v) Echunga Clay, T.

This clay is capable of activation to a high degree, although the products have not proved as good as the best obtainable from Pt. Willunga and Hackham clays. Acid required for treatment would be approximately 850 lb. of sulphuric acid per short ton of raw clay.

(vi) Ochre Point Clays, V and W.

These were kaolinite clays, and their low natural activities, and negligible response to acid treatment were therefore to be expected.

6. REFERENCE.

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