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- RESEARCH AND DEVELOPMENT BRANCH -

CHEMICAL RESEARCH SECTION

REPORT No. R.D. 8.

"CHEMICAL BENEFICIATION OF WHITE CLAYS"

by

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SUMMARY.

Chemical beneficiation has been examined as a means of improving the whiteness of clays from Tea-tree Gully, Mt. Crawford and Birdwood.

It has been concluded that such treatment would be uneconomic for these clays.

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1. INTRODUCTION :

In many industrial applications such as in paper manufacture the suitability of a clay is dependent upon its color, the most acceptable clays being those which are almost pure white.

Some local clays have a restricted use in industry because they are below the required standard of whiteness. Reduction or elimination of their color by some simple chemical treatment was considered as a means of extending the usefulness of such clays. This report describes some preliminary work carried out on three local clays.

2. MATERIAL EXAMINED :

The four samples of clay examined in this investigation were elutriated products prepared by the Metallurgy Section.

The samples were approximately 500 g. in weight, and were described as follows :-

Sample No.	Description.	
M.37	Tea-tree Gully	- final washed product.
M.38	Mt. Crawford	- " " "
M.39	Birdwood	- fine washed product.
M.40	Birdwood	- coarse washed product.

3. EQUIPMENT :

3.1 - Leaching tests were carried out in 400 ml. and 600 ml. beakers, relying on the agitation caused by boiling to keep the clay suspended in the reagent solution. Vacuum filtration on Buchner funnels was found to be satisfactory and reasonably rapid. Products were dried in an air oven at 60° to 70°C., and the dried products re-ground in a Wedgwood mortar.

3.2 - To obtain accurate comparisons of the degree of whiteness of the products, a G.M. Mark II fluorimeter was modified for use as a reflectance meter. By suitable adjustment of sensitivity, it was found possible to set the instrument to give zero reading with an empty slide, and full scale deflection with finely ground magnesium carbonate packed into a platinum dish and placed in the slide. Clay products were similarly placed in the instrument and the reflectance was read directly as a percentage of that obtained from magnesium carbonate.

3.3 - Ignition tests were carried out in porcelain crucibles in an air atmosphere muffle (nichrome wound) at temperatures up to 950°C.

4. ANCILLARY MATERIALS :

Tests were carried out using hydrochloric acid, nitric acid, sulphuric acid with sodium fluoride, sodium carbonate, sodium bi-carbonate, sodium hydroxide, sodium sulphite, sodium nitrite and bleaching powder (chloride of lime) as possible leaching or bleaching agents.

Finely ground magnesium carbonate (A.R. grade) was used as a standard of 100 per cent reflectance.

5. EXPERIMENTAL PROCEDURE :

5.1 - Leaching.

Preliminary tests in the Metallurgical Laboratories, using dilute sulphuric acid with and without reducing agents such as sodium sulphite, had been unsuccessful. It was decided, therefore, to employ more drastic treatment initially than would be desirable commercially and if any treatment were successful, then the minimum concentration of reagent and other conditions necessary could be determined.

The procedure adopted consisted of boiling the sample with the various reagents, at a pulp density of 5 per cent solids, for 45 minutes to 1 hour. The hot solutions were filtered on a Buchner funnel and the residues washed several times with water, dried at 60° - 70°C., re-ground and then compared with the originals, both visually and by reflectance measurement.

5.2 - Reflectance measurements.

Using the modified G.M. Mark II Fluorimeter, reflectance measurements were made on the clay products and on the samples as received. Samples were packed into platinum dishes (1.5 cm. diameter) using a spatula to obtain a surface as smooth and level as possible. Constant checks of the zero and 100 per cent setting of the instrument were made using the empty slide, completely blackened, as zero, and a dish packed with magnesium carbonate as 100 per cent. A standard deviation in precision of the order of 1.5 per cent was obtained from these measurements, using a freshly-packed platinum dish for each reading. This was considered to be sufficiently accurate to enable comparisons to be made.

5.3 - Ignition tests.

Although it was appreciated that ignition of the clays would destroy their desirable properties for use as fillers, some of the prepared products together with the original samples were ignited for an hour at 950°C. in an air atmosphere muffle in open porcelain crucibles. The colour of the ignited products gave an indication of the amount of iron remaining. In some cases the whitening of the sample by ignition showed that the coloration of the clay or product was not due to iron.

6. EXPERIMENTAL RESULTS :

6.1 - Visual Comparison.

Table 1 indicates the appearance of products obtained by treatment with the reagents shown.

6.2 - Reflectance Measurements.

Table 2 shows the reflectance of the clays and some of the products, expressed as a percentage of the reflectance obtained from finely ground magnesium carbonate (A.R. grade).

TABLE 1.

PHYSICAL APPEARANCE OF TREATED CLAY.

REAGENT.	APPEARANCE OF PRODUCT.			
	M.37	M.38	M.39	M.40
Nil.	light fawn	off-white	light cream	light cream
1 $\underline{N}$ HCl	light grey	slightly improved	very slightly improved	very slightly improved
1 $\underline{N}$ HCl + 5% chloride of lime	" "	" "	" " "	" " "
2 $\underline{N}$ HCl	" "	" "	" " "	" " "
1 $\underline{N}$ H_2SO_4 + 1 $\underline{N}$ Na_2SO_3	no change	no change	no change	no change
1 $\underline{N}$ H_2SO_4 + 0.01 $\underline{N}$ NaF	light grey	slightly improved	very slightly improved	very slightly improved
2 $\underline{N}$ H_2SO_4 + 0.1 $\underline{N}$ NaF	" "	" "	" " "	" " "
1 $\underline{N}$ HNO_3	-	-	" " "	-
1 $\underline{N}$ HNO_3 + 5% $NaNO_2$ (added over the period)	-	-	" " "	-
1 $\underline{N}$ Na_2CO_3	slightly darker	no change	no change	no change
1 $\underline{N}$ $NaOH$	-	-	" "	-
1 $\underline{N}$ $NaHCO_3$	-	-	" "	-
2 $\underline{N}$ HCl followed by 1 $\underline{N}$ Na_2CO_3	light grey	slightly improved	very slightly improved	very slightly improved

TABLE 2.

EFFECT OF CHEMICAL TREATMENT.

REAGENT.	REFLECTANCE (%)			
	M.37	M.38	M.39	M.40
Nil	80	90	87	78
1 N HCl	81	96	91	81
2 N HCl	82	97	92	82
2 N HCl followed by 1 N Na_2CO_3	82	96	92	82
1 N H_2SO_4 + 0.01 N NaF	80	96	89	81
2 N H_2SO_4 + 0.1 N NaF	-	-	91	-
1 N HNO_3	-	-	90	-
1 N Na_2CO_3	78	92	89	79
1 N NaOH	-	-	87	-

6.3 - Effect of Ignition.

Table 3 lists the changes, judged visually, which occurred on ignition at 950°C. of portions of the products for one hour in air.

TABLE 3.

CHANGE IN COLOUR ON IGNITION.

REAGENT	M.37	M.38	M.39	M.40
Nil	fawn to pink.	off-white to very light pink	light cream to light pink.	light cream to light pink.
1 N HCl	light grey to cream.	off-white to white.	light cream to off-white.	light cream to off-white.
1 N Na_2CO_3	fawn to pink.	off-white to very light pink.	light cream to light pink.	light cream to light pink.
1 N H_2SO_4 + 0.1 N NaF.	light grey to cream.	off-white to white.	light cream to off-white.	light cream to off-white.
1 N NaOH			light cream to light pink.	
1 N HNO_3			light cream to light pink.	

7. DISCUSSION :

It was considered that the most likely causes of colour in these clays were :-

1. iron, as limonite.
2. organic matter.
3. other coloured minerals.

While colour due to certain refractory mineral impurities would not be easily removed, it was considered that acid leaching would remove limonitic iron if present and that carbonate leaching would probably attack organic matter.

An examination of the results tabulated above shows that some improvement of all samples was obtained by leaching with hydrochloric acid or with sulphuric acid and fluoride. Although the colour changed, Sample M.37 gave very little improvement in reflectance. However, ignition tests confirmed that most of the iron had been removed, that is, the pink colour due to ferric oxide did not develop on ignition, although a cream colour still remained after ignition.

Samples M.39 and M.40 behaved similarly, and much less colour remained after ignition. In these three samples it is evident that part of the coloration is due neither to limonitic iron nor to organic matter as it is not destroyed by acid digestion or by ignition. There appears to be no likelihood of obtaining satisfactory improvement of these samples by leaching.

The best improvements in reflectance for all samples were obtained with 2 normal hydrochloric acid. Retreating the same samples with 1 normal sodium carbonate to remove any further organic matter showed no further improvement, although with Samples M.38 and M.39, direct sodium carbonate leaching had produced a slight improvement in reflectance. It is apparent that any organic matter dissolved by sodium carbonate solution is also dissolved by acid leaching.

Sample M.38 was the whitest clay of the four received and also showed the maximum improvement in reflectance by acid leaching, namely from 90 to 97 per cent. The acid-treated products when ignited were almost pure white, indicating that the colour remaining was possibly due to organic matter. However, a re-treatment, using sodium carbonate, did not improve the reflectance, and the use of bleaching powder with hydrochloric acid made no difference to the product. It is apparent that the remaining colour is difficult to remove by means other than ignition.

Sample M.37 showed no significant improvement with acid, alkali or bleaching agents.

Sample M.38 was improved to a large extent by acid treatment, but the remaining colour could not be removed except by ignition.

Samples M.39 and M.40 were improved to a small extent by acid leaching but the result was not considered to be significant, the best reflectance measurements being 92 and 82 per cent respectively.

In general, no improvement was obtained with oxidising or reducing agents such as bleaching powder or sodium sulphite. Alkaline treatments were also not effective. Of the acid treatments, hydrochloric acid was the most effective, although sulphuric acid with sodium fluoride was almost as good. The effectiveness of 2 normal acids was little better than 1 normal acids and it is likely that much weaker acid could be used on a clay amenable to treatment, such as Sample M.38.

As no significant general improvement was achieved with these four samples, the further work necessary to determine the minimum acidity required for leaching was not carried out.

8. PRACTICAL APPLICATION :

The results indicate that only in the case of Sample M.38 is a leaching treatment likely to give a significant improvement in the degree of whiteness of the clay.

No accurate estimate can be made of the total cost of such treatment but the cost of leaching with 1 normal hydrochloric acid would be of the order of £4 per ton of clay treated, as shown below :-

Assumptions:-

Cost of concentrated hydrochloric acid	£40 per ton.
Leaching solution	1 normal hydrochloric acid.
Pulp density	30 per cent solids.
Acid available for re-cycling	50 per cent of original.

Calculations:-

In 100 lb. of pulp, 30 lb. clay is leached with 70 lb. 1 N HCl.

Acid consumption is then 35 lbs. 1 N HCl per 30 lb. of clay treated, equal to approximately 3 lbs. conc. HCl per 30 lb. clay or 200 lbs. acid per ton of clay.

Cost of hydrochloric acid = £4 per ton of clay treated.

Sulphuric acid and fluoride leaching would probably be somewhat cheaper depending on the availability and cost of fluorite (CaF_2) or other fluoride.

It is considered that the materials cost would probably be uneconomic unless a greater degree of improvement than that indicated by the above tests was obtained.