ENCLOSURE (B)

ENCLOSURE (B) 1

STUDIES ON THE ACID CLAY

by

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Research Period: 1940-1942

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

It was the object of this research to find 1) the most reactive clay catalyst in our territory for use in catalytic cracking and 2) the most desirable conditions for activation. Typical clays produced in Japan were tested for effectiveness in catalytic cracking, and acid clay gave the most satisfactory results. The activating conditions of several acid clays selected from various sources were studied, using sulphuric acid as activating agent. An acid clay produced near KOMATSU City, ISHIKAWA Prefecture gave the best result. This catalyst was used in the commercial plant at YOKKAICHI, Second Naval Fuel Depot.

I. INTRODUCTION

This research was carried out from December, 1940 to August, 1942 in cooperation with Takeda Acid Clay Co. Ltd. at MIZUSAWA, YAMAGATA Prefecture, by Lt. Eng. M. MURAKAMI and Assist. Eng. M. MIYASAKI and Eng. J. ISHIKAWA, the latter being a representative of the company.

II. DETAILED DESCRIPTION

A. Apparatus

The activity test apparatus for catalytic cracking catalysts is shown in Figure 1(B)1.

B. Procedure

A definite kerosene fraction of Midway crude oil was selected for use in the catalyst activity tests.

150cc of the oil was passed into the reaction tube containing 100cc of catalyst, at a constant rate for 1.5 hours (space velocity 1.0). Reaction conditions were held constantly at a temperature of 450°C, and atmospheric pressure for all catalyst samples. Reaction products were distilled using an Engler distillation flask, and fractions boiling up to 150°C were collected and measured. The catalyst activity of our experiments were compared by the term "decomposition rate", which is expressed as the volume % of the fraction boiling up to 150°C to the initial charge. Analyses of the composition and activity of many kinds of natural clays produced in Japan were made.

C. Results

Results of typical tests are shown in Table I(B)1. These results show that acid clays give higher activity than the others and that there is no linear relation between activity and composition.

Several samples of acid clays were activated by boiling for 3 hours with sulphuric acid, having concentrations varying from 1 N to 7.5N, so that changes of activity and chemical components could be observed. The experimental results were as tabulated in Table II(B)1.

III. CONCLUSIONS

From these results it was concluded as follows:

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The activity of acid clay is not dependent on its chemical components, but on its origin.

It seems, in general, that the clays which have high content of MgO show high activity.

The molecular ratio SiO_2/Al_2O_3 of the activated acid clays showing maximum activity appears generally to be approximately 6.

Best normality of H_2SO_4 for activating acid clays for use as catalysts lies between 1 to 4.5 N as compared to that of activating acid clays for use as adsorbent in decolouring petroleum or fatty oils, which varies from 3 to 6 N H_2SO_4 according to the origin of the clay.

The acid clay produced near KOMATSU City was activated by Takeda Acid Clay Co., Ltd., and has been used in the commercial catalytic cracking plant at the Second Naval Fuel Depot.

It is also suitable for use in the catalytic reforming of pine root oil. Experimental results for this application are given in another report.

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Table I(B)1
COMPOSITION, SOURCE, AND CATALYTIC EFFECT OF TYPICAL CLAYS

Name of Clay	Source	Component									Activity Test
		Ign. loss	SiO_2	Al_2O_3	Fe_2O_3	MnO_2	CaO	MgO	SO_3	P_2O_5	Decomposition rate (%)
Diatomaceous Earth	FUDOSAN, Ureshino Saga Prefecture	9.5	72.8	11.7	3.7	0.9	0.7	trace	0.6	trace	4.4
Bentnite	SHIRIKUKIYUMANAI, Hokkaido	5.0	74.8	13.9	2.5	trace	2.3	2.2	0.2	0.1	6.5
Acid clay	KOMATSU City, Ishikawa Prefecture	11.0	61.8	21.7	2.1		0.7	4.3			16.7
Acid clay	NAKAJO, Niigata Prefecture	7.1	74.0	14.0	2.0	0.0	1.8	2.8	0.0	0.0	10.0
Acid clay	MIZUSAWA, Yamagata Prefecture	11.1	73.2	17.1	0.1	trace	0.1	1.8	0.1	trace	11.9
Kaoline	HOKUTO, Taihoku City, Formosa	14.9	42.6	39.1	4.2	0.6	0.7	0.2	2.5	0.0	1.4

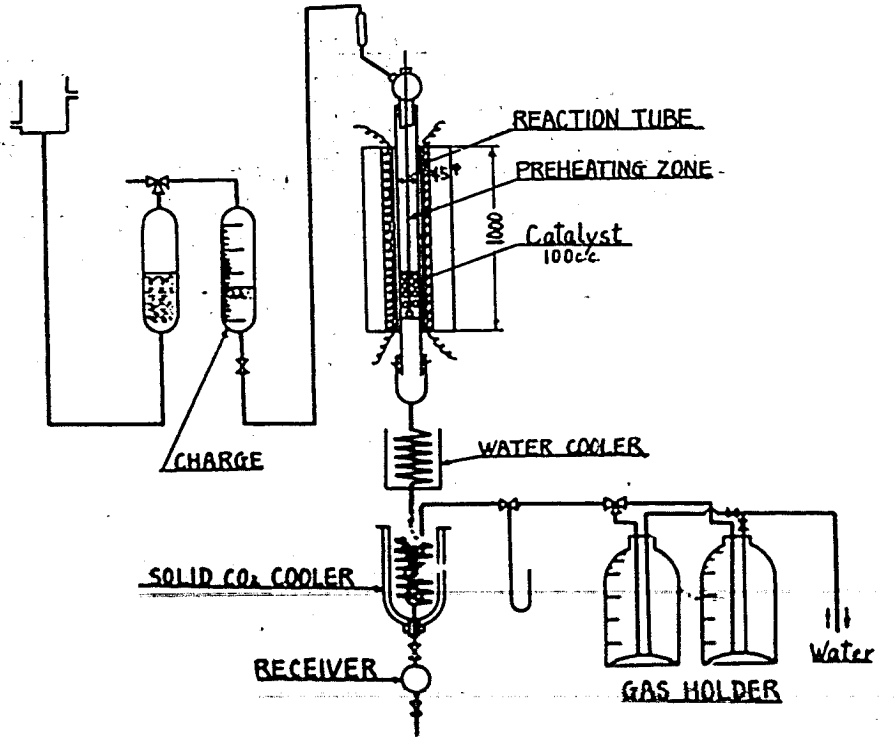

Figure I(B)1
APPARATUS FOR TESTING ACID CLAY CATALYSTS

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Table II(B)1
EFFECT OF ACID TREATMENT ON TYPICAL CLAYS ON COMPOSITION AND ACITVITY

	Conc of H_2SO_4 for activation	Component						Activity test
		ign loss	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	Decomposition rate (%)
Acid Clay from IZU	non treated	12.3	29.0	50.7	5.1	0.3	2.9	9.6
	1 N	12.0	28.8	52.2	4.9	0.3	2.6	12.0
	2 N	11.4	25.7	55.4	4.6	0.1	2.5	14.3
	3 N	11.1	22.6	60.6	4.1	0.2	1.3	17.4
	4.5 N	9.0	15.8	70.7	3.7	0.1	1.0	18.2
	6 N	8.6	14.0	74.2	1.3	0.1	0.8	13.5
	7.5 N	7.4	8.8	81.2	1.3	0.1	0.5	
Acid Clay from MIZUSAWA	non treated	8.4	24.5	59.1	4.0	0.7	2.7	8.8
	1 N	8.5	24.5	60.1	3.6	0.7	2.8	11.6
	2 N	8.1	20.7	66.1	2.9	0.8	2.5	15.5
	3 N	7.2	17.2	68.3	3.1	0.8	2.5	14.7
	4.5 N	6.4	11.3	75.7	2.3	0.6	1.7	9.6
	6 N	5.2	7.4	81.3	1.5	0.7	1.1	
Acid Clay from KOMATSU	non treated	11.0	21.7	61.8	2.1	0.7	4.3	16.7
	1 N	7.0	17.9	70.3	1.4	0.6	3.9	17.7
	2 N	6.9	16.2	70.9	1.2	0.6	3.5	20.3
	3 N	6.5	13.9	76.0	1.1	0.5	2.3	13.4
	4.5 N	5.4	10.1	82.4	0.7	0.5	1.7	17.0
	6 N	4.2	3.3	91.0	0.7	0.5	0.7	12.4
	7.5 N	5.2	0.8	92.7	0.4	0.4	0.3	
Acid Clay from SONCHOYAMA	non treated	10.3	21.2	58.7	4.1	1.4	4.8	16.1
	1 N	8.8	20.3	61.2	3.1	0.5	4.6	17.8
	2 N	8.1	20.3	64.6	2.5	0.4	4.0	22.0
	3 N	7.5	16.7	70.0	2.2	0.3	3.0	15.3
	4.5 N	6.9	14.2	74.2	1.8	0.4	2.5	13.4
	6 N	6.8	7.1	82.1	1.3	0.3	1.1	7.4
	7.5 N	6.8	4.1	86.3	0.7	0.2	0.4	
Acid Clay from NAKAJO	non treated	9.4	20.1	64.1	2.4	0.6	3.5	17.5
	1 N	7.8	19.2	66.3	2.2	0.4	3.4	21.2
	2 N	7.2	18.7	66.9	2.0	0.4	3.3	19.3
	3 N	6.9	13.7	72.1	1.9	0.4	2.9	16.4
	4.5 N	5.3	7.4	82.4	1.3	0.3	2.9	9.7
	6 N	3.8	7.0	87.1	0.3	0.3	1.4	8.2
	7.5 N	3.7	2.1	92.4	0.3	0.3	1.1	
Bentnite from YAMAGATA	non treated	5.1	20.2	67.4	3.6	1.7	2.4	14.6
	1 N	6.1	20.0	69.3	2.6	0.7	1.4	14.0
	2 N	6.1	19.9	70.1	2.3	0.6	1.2	14.6
	3 N	6.4	19.3	71.1	2.1	0.6	1.1	14.0
	4.5 N	6.2	16.6	73.4	2.0	0.6	1.0	13.1
	6 N	5.9	13.3	76.5	2.0	0.5	0.9	
	7.5 N	4.7	10.7	79.2	1.6	0.5	0.8	
Acid Clay from MATSUMA	non treated	5.7	13.1	75.8	1.3	1.6	3.5	12.3
	1 N	5.7	12.6	76.7	1.3	0.4	2.6	16.5
	2 N	5.0	11.6	78.7	1.2	0.4	2.3	14.2
	3 N	5.1	10.9	80.0	1.0	0.4	2.1	14.3
	4.5 N	4.3	9.6	83.2	1.0	0.3	1.6	12.7
	6 N	4.2	3.2	88.9	0.5	0.3	0.8	10.6
	7.5 N	3.3	2.3	92.5	0.1	0.2	0.4	