DAEHAN HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 16, No. 3, 1972
Printed in Republic of Korea

국산 벤토나이트 그리이스 제조

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한국과학기술연구소
(1972. 4. 16접수)

Grease from Korean Bentonites

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(Received April 16, 1972)

요 약 : 국산 벤토나이트를 분자량이 큰 imidazolines과 반응시켜 벤톤을 만들었으며 벤토나이트의 양이온 교환율이 100meq/100g이상이 됨을 알았다. 제조한 벤톤은 윤활유에 분산시키고 three-roll mill로 milling한후 그리이스를 만들었다. 이들 그리이스의 주도 (microscale로), 정상상태에서의 산화 안정도, 내수성, 및 내 마모성은 ASTM방법에 의하여 시험하였고 매우 좋은 실험결과를 얻었다.

Abstract : Bentones from Korean bentonites were first prepared by reacting bentonites with high molecular weight imidazolines. The cation exchange capacity of bentonites was found more than 100meq/100g sample. Greases were then prepared by dispersing bentones into a lubricating oil and milling through a three-roll dispersion mill. Consistency in microscale, oxidation stability (static), water resistance, and wear property of the greases were tested by the ASTM methods, and good experimental results were obtained.

Introduction

Bentonite or, more accurately, montmorillonite is a hydrated magnesium aluminum silicate and it is used for the production of bentone. The most typical bentones are Wyoming type in which the cation is mainly sodium. When montmorillonite is hydrated in a very dilute dispersion, the platelets separate to their unit particles and each platelet orients water molecule around it in a hexagonal configuration, forming a thixotropic gel of montmorillonite in water. The reactive sodium atoms of the unit plates may be replaced by suitable organic cations[1,2]. Dispersions of sodium bentonite in water have been treated with the salts of amino-compounds containing not more than six carbon atoms forming hydrophilic organic ammonium bentonites[3]. Most bentone greases, mixtures of such bentones and various lubricating oils, are prepared from this Wyoming type clay.

There does not appear to be any previous account of bentone greases from Korean bentonites which are essentially the same clay as the Wyoming type, except the cation is potassium rather than sodium. Korean bentonites, however, do not hydrate in a dilute dispersion and tend to minimize swelling in water. These unusual characteristic of Korean bentonites make the separation of inorganic impurities, mica, silica, etc. from a crude clay difficult and the cation exchange capacity cannot be determined under these circumstances. Since the conventional process of manufacturing organophilic bentonites with the Wyoming type cannot be applied on the Korean bentonites, a new process is developed for the Korean bentonites.

Comparison between nonsoap thickened greases, clay thickened greases, and metallic soap greases cannot, of course, be made on the basis of what are considered satisfactory products. Greases from Korean bentonites, however, seemed to be good quality for high temperature operation.

Experimental

Organophilic bentonites Two types of Korean montmorillonite ore (A and B) were selected and crushed with a ball mill up to 200 mesh. The powder was dispersed in water to separate from non-clay impurities. The pH of water solution was fixed at 10. 2–10. 4 with tetrasodium pyrophosphate. Non-clay impurities were easily separated from the clay and removed by decantation. The dispersion was then treated with HCl salts of imidazolines using 100meq/100 g sample quantities. The gel formation (coagulation) of organophilic bentonites was filtered, dried at 80 °C, and powdered with a alumina-ball mill.

Greases Mineral oil equivalent to SAE 50 was used as a base oil. 10–20 % organophilic bentonites were mixed with certain amount of base oil to produce greases whose final consistencies fall into NLGI 2 and 3. A mixture of methanol, cetanol, and tolune was used as a dispersant at the same time. The mixture was processed with a three-roll mill and deaerated in vacuum. No additives were used throughout the experiment.

Measurements and Tests The consistency of organophilic bentonite greases was measured using a micropenetrometer (*Fig.* 1). 5 grams of sample greases were taken in a sample holder and a needle of definite shape was dropped from the surface for 5 seconds. The penetration was then corrected to the ASTM penetration using a linear relation between the ASTM and micro penetrations as shown in *Fig.* 2. The oxidation

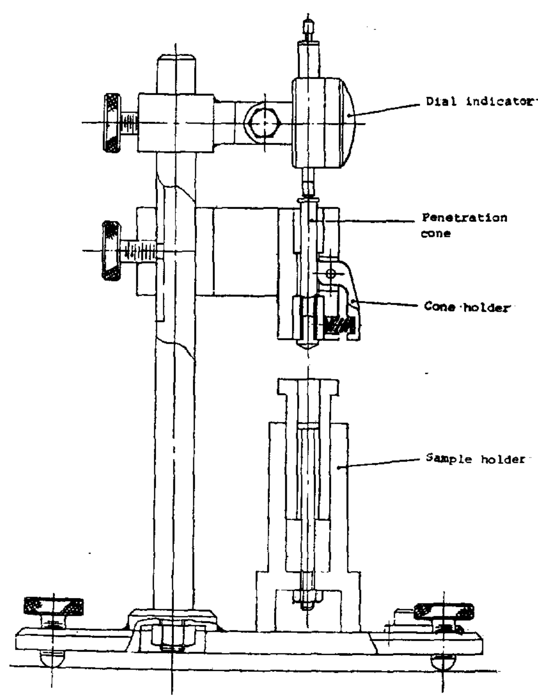


Fig. 1 Micro-Penetrometer

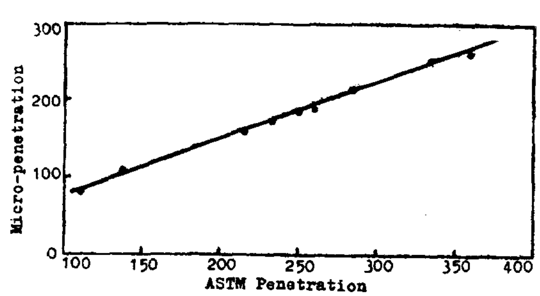


Fig. 2 ASTM Penetration *vs* Micro-Penetration stability of organophilic bentonite greases was measured by the ASTM D942 method for 100 hrs at 210 °F.

The grease water-washout test was performed by the ASTM D1264 method for 1 hr at a speed of 600±30 rpm. Water at 100 °F was applied through an orifice at a speed of 5±0.5 ml/sec. A Shell four-ball wear test was made at 40 kg load, 1200 rpm, and 75 °C for 1 hr. Wear scar diameters on the balls were measured by a microscope.

Results and Discussion

Montmorillonite is composed of silicon and oxygen atoms which are linked together in a tetrahedral arrangement as shown in *Fig.* 3. Water molecules, adsorbed between layers, are normally associated with the oxygen atoms of the lattice or with metallic ions in the layer. When a montmorillonite is dispersed in water,

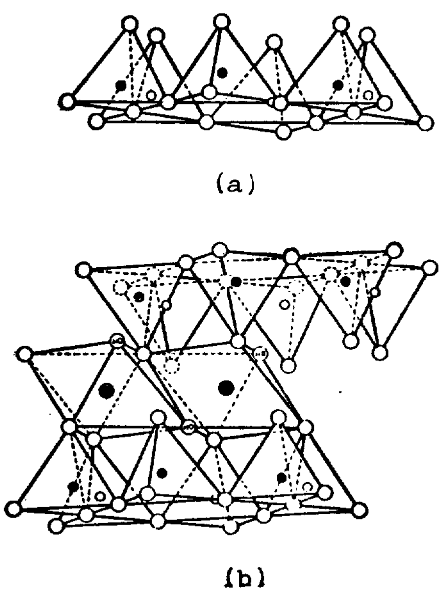
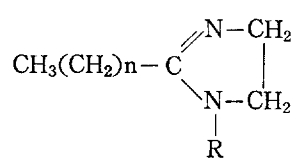


Fig. 3 Crystal Structure of Montmorillonite
(*a*) Tetrahedron Linkage
(*b*) Layer Structure
○ Oxygen ● Aluminium, Iron, Magnesium
○ or ● Silicon (or Aluminium)

bonding force between layers becomes smaller due to the association of polar water molecules with the negatively charged oxygen surface, resulting an appreciable volume change. Non-clay impurities (chemical compositions of Korean ores were analyzed as follows: 60∼70 % of SiO_2, 13∼17 % of Al_2O_3, 3∼5 % of Fe_2O_3, ∼1 % of CaO, ∼1 % of MgO, and ∼10 % of ignition loss) were first separated by dispersing the bentonite in water, and the structure of pure bentonite was checked by X-ray diffraction, as shown in *Fig.* 4. The pattern was compared with that of Wyoming bentonite[4] and the cation was found to be potassium. When alkyl ammonium salt ware used as organophilic meterials, they exchange with metallic ions and the clay becomes organophilic in nature. Thus, in modified or treated clays, alkylammonium ions replace metallic cations, and are ionically bended to the clay structure. If long chain amines are used, the resulting organophilic bentonite becomes more oleophilic in nature. Amine compounds, therefore, of imidazolines, which may be represented as



where R is a relatively low molecular weight substituent (ethyl radical) while the alkyl grouping contains more than ten carbon atoms, were selected in this experiment. The imidazolines were treated with ammonium acetate and ammonium chloride in order to form the corresponding quaternary ammonium salts. The cation exchange capacity of bentonites was measured by dispersing 100 g clay in 3 l water, reacting with the amine, and settling for 3 hrs.

The average exchange capacity was more than 100 meq/100 gram sample, both for clay samples

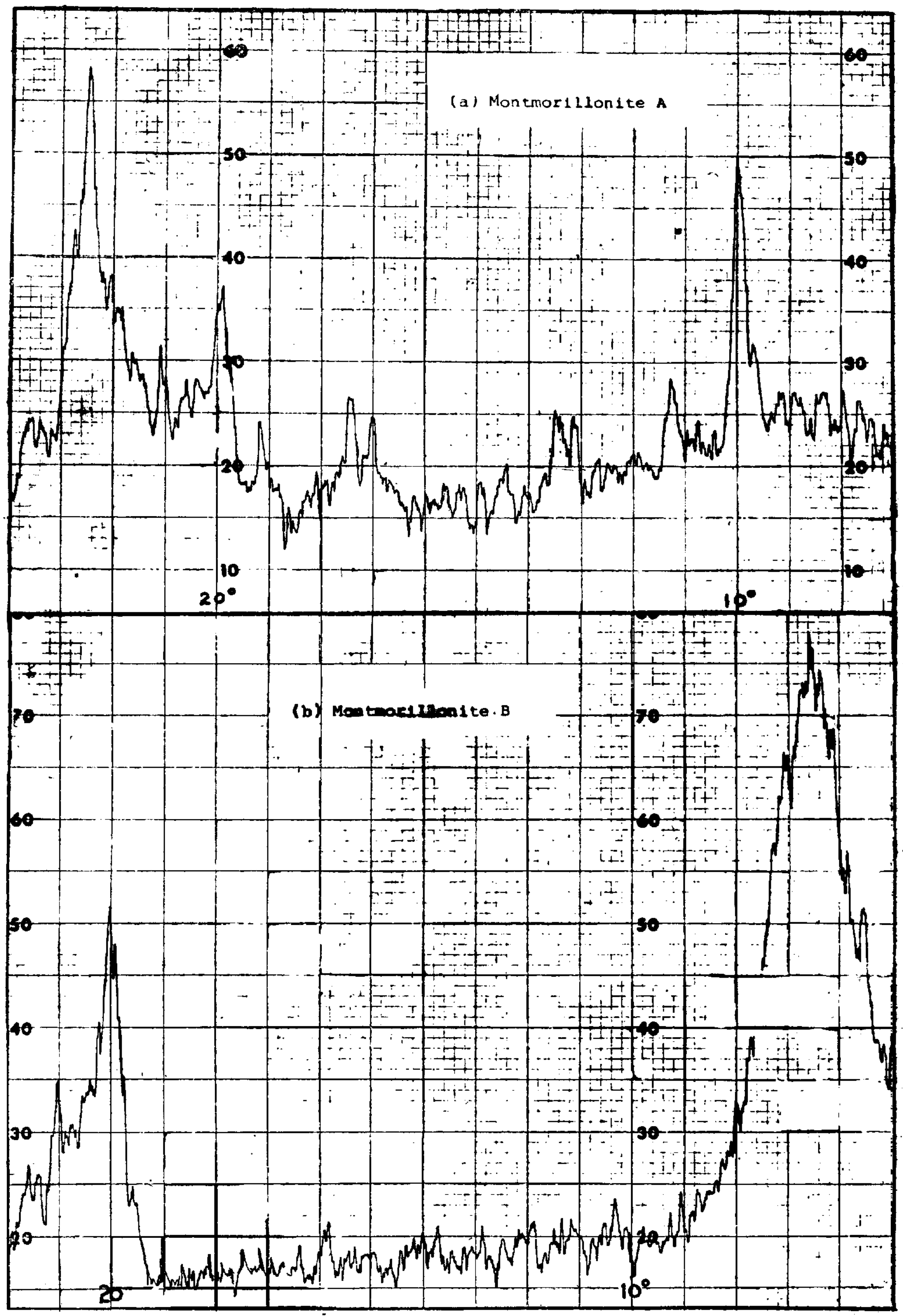


Fig. 4 X-ray diffraction

Table 1. Base exchange capacity of some organophilic compounds

Organophillic Compound (amine constituent)	Base Exchange Capacity, meq/gram sample
benzidine[5]	0.91
p-phenylenediamine[5]	0.86
α-naphthylamine[5]	0.85
p-aminodimethylaniline[5]	0.95
2, 7-diaminofluorene[5]	0.90
piperidine[5]	0.90
imidazoline (bentnite *A*)	1.10
imidazoline (bentonite *B*)	1.20

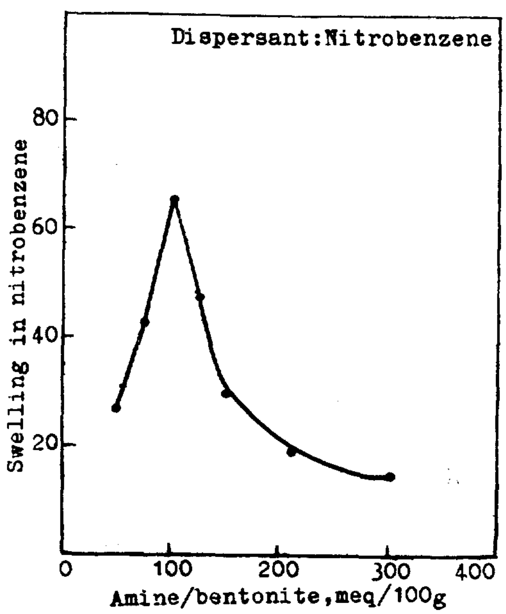


Fig. 5 Effect of Varying Ratio of Cation to Bentonite upon Swelling in Nitrobenzene

A and B, and the results were compared with other amine constituents[5] as shown in *Table* 1. When a gel of bentone is prepared, an organic liquid can be used as a dispersant to enhance the swelling effect of a bentone. The effect normally depends on the type and quantity of liquid used, as shown in *Fig.* 5[1].

A mixture of methanol, cetanol, and toluene was used in the experiment and it was found

Table 2. Effect of oil composition on bentone grease consistency

Oil Viscosity, SUS		*V. I.*	Gravity, °API	Unworked Penetration
@100 °F	@210 °F			
73.1	35.9	−29	27.6	217
184	45	94	31.4	213
294	50.8	86	26.5	316
312	53	91	29.9	229
480.5	53.1	20	21.6	230
572	55.7	18.4	21.8	213
808	78	93	30.0	211
1183	72	14	20.6	214
2475	148	94	27.2	194
6040	148	−7	16.9	333

Table 3. Physical properties of base oil(SAE 50 grade)

Viscosity, SUS, at	100 °F	1120
	210 °F	90
Viscosity Index		88
Gravity, °API		24.7
Flash Point, °F		489

an amount equal to 10 % of bentone weight was an ideal quantity. Since a long chain amine was used, a good swelling effect was obtained. Compouds other than alkyl ammonium salts, such as "amido-compounds", can be used as modifying agents[6,7], and an ammonium dimethyl dibenzyl or ammonium dimethyl dioctadecyl bentonite clay was also manufactured by Butcosk[8].

The consistency of a grease depends primarily on a viscosity of base oil. The consistency normally falls in the same range if the viscosity of base oil is about the same range, as shown in *Table* 2[9]. Referred to this table, a base oil equivalent to SAE 50 whose physical constants are shown in *Table* 3 was used in these experiments.

It was possible to make greases of NLGI grades 2 and 3 with the oil even though the consistency varied little with the type and amout of bentone. Since a volume change of organo-

Table 4. Penetration of bentone greases

Sample*	Bentone %	Penetration
J T D	10	357
J T D	15.6	260
J T D	20	109
J A C	10	337
J A C	20	214
J A T	10	286
J A T	20	251
K T D	15.5	233
K T D	20	219

* K: Korean bentonite
J: Japanese bentonite
TD: tetradecylamine
AC: undecylamine
AT: tertiary amine

Table 5. Oxidation stability of bentone greases

Sample*	Pressure Drop, psi**
K A C	4.5
K A T	9.0
K B B	7.5
K A O	4.5
K B Y	6.5
K B Y***	6.0

*BB: hexadecylamine
AO: heptadecenylamine
BY: mixture of amines
**210 °F, 100 hrs
***Anti-oxidant added

Table 6. Water washout test of bentone greases

Sample*	Greases Loss, Wt %
J T D	1.25
J A C	2.95
J A T	2.00
J A S	1.99
J A O	1.98
K T D	1.98
K A O(1)	7.51
K A C	2.00
K A T	0.75
K B B	1.00
K B Y	7.00
K A O(2)	1.00

* AS: heptadecylamine

Table 7. Wear test of bentone greases

Sample	Wear Scar Diameter, mm*
J T D	0.740
J A C	1.352
J A T	0.908
J A S	0.956
J A O	0.680
K T D	0.956
K A O(1)	1.016
K A C	1.208
K A T	1.024
K B B	0.972
K B Y	0.748
K A O(2)	0.724

* load=40 kg, speed=1,200 rpm, time=1 hr

philic bentonite increases when amine compound is replaced in a double layer of clay, it is known fact that a swelling is accompanied by a decrease in consistency of the resultant grease. The relation between the penetration and percent bentone is shown in *Table* 4, and a maximum of 20 % bentone was sufficient to make greases of NLGI grade 3–4.

Other properties of bentone greases succh as the effect of temperature on consistency, bleeding effect, and shear stability of bentone grease are normally better than those of conventional metallic greases. The retention of bentone grease to metals is also better than that of metallic greases. This fact was indirectly confirmed by a simple burning of greases with a match. Metallic soap greases drip from a metallic plate as they burn, while bentone greases ash without dripping. This simple experiment also shows the high dropping point of bentone greases.

Oxidation stability, water washout, and wear tests were made by the ASTM methods and the results are shown in *Tables* 5, 6, and 7. Less than 10 psi drop was observed from the oxidation stability test, indicating a good stability of oxidation. In one case, an anti-oxidant was added, and yet no appreciable change was obtained. Water washout test also showed good results with less than 3 wt. % loss in most cases. This property of Korean bentone greases was compared with that of bentone greasese from Japanese bentonite, and the result was somewhat better with the former. The same comparison was made for the wear characteristics, and an average of ~0.900mm wear scar diameter was obtained for both greases.

Conclusion

There are five major factors which affect the quality of bentone greases: 1) quality of raw materials-bentonite and base oil, 2) particle size of bentonite and bentone, 3) nature of dispersants, 4) nature of organophilic compounds, and 5) percentage of bentone. There is no need to say about first factor. One can choose either Wyoming type or Korean bentoite. If Korean bentonite is used, the cation of the clay must be replaced by sodium ion using the aforesaid treatment prior to amine treatment. Since the reaction between clay and amine depends largely on the surface of clay, it is necssary to have micronsize particles. Even the nature of dispersing agent does not significantly affect the nature of the grease, but a selection of right agent becomes crucial sometimes. One can produce several types of bentone greases according to the type of organophilic compounds. Alkylammonium salts derived from amine compounds, however, seemed to be very useful and these must include long chain carbon atoms to increase the swelling effect. Alkylammonium salts from tertiary amines are more effective than those from secondary or primary amines due to the spatial structure of tertiary amines.

The consistency of bentone greases partially depends on the amount of bentone, but less than 20% bentone is sufficient for greases of NLGI grade 3 or 4.

Acknowlegents

The authors wish to thank Dr. S. L. Cosgrove of the University of Cincinnati for his advice and counsel in this work.

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