

# Modified smectitic Tunisian clays used in the formulation of high performance lubricating greases

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## Abstract

Two smectitic Tunisian clays were organically modified by exchange reaction with dioctadecyl dimethylammonium chloride (DODMA) and hexadecyl benzyl dimethylammonium chloride (HBDMA). The resulting organoclays were used in the formulation of lubricating greases. The results of the performance tests applied to the obtained greases showed that their physicochemical and mechanical characteristics are in conformity with the extreme-pressure (EP) greases specifications. The obtained greases present good EP properties with only 0.5% EP additives. The smectitic clays used could constitute a raw material in the formulation of high performance lubricating greases.

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## 1. Introduction

Lubricating grease is a semisolid product resulting from the fine dispersion of a thickening agent in a lubricating oil (Jolicœur, 1992). The thickening agent is generally a metallic soap prepared by saponification of a fatty substance, but can be also a non-soap product such as polyurea (Baily, 1985) or organoclay.

Due to their ability for swelling and gel formation in organic media, organoclays have found a wide application in industry as structure-forming and thickening agents in inks, paints, cosmetics, drilling fluids and lubricating grease formulations (Grandou and Masson, 1996; Murray, 2000; Avci, 2003). The use of organoclays as thickening agents in lubricating grease formu-

lations confers to the greases excellent thermal stability and high performance qualities (Oswald, 1982; Christian, 1983; Magauran, 1987; Morita, 1991; Dennis, 1998).

Organoclays are prepared by organophilic modification of smectite-type clays having cation exchange capacities (CEC)  $\geq 70$  meq  $100\text{ g}^{-1}$  (Dennis, 1998). The organic modifiers mostly used are tetra alkylammonium compounds of the general form  $[(\text{CH}_3)_3 \text{NR}]^+$  or  $[(\text{CH}_3)_2 \text{NRR}']^+$  where  $R$  is a large alkyl chain from 12 to 18 carbon atoms (Oswald, 1982; Magauran, 1987; Morita, 1991). The cationic exchange between these ions and the interlayer exchangeable inorganic cations on clay mineral surface, provides the clay organophilic character (Bergaya and Lagaly, 2001; Koh and Dixon, 2001).

The dispersion of organoclays in lubricating oil is described as the mechanism which separates the individual agglomerated organoclay particles. Dispersion is typically accomplished by the use of polar activators

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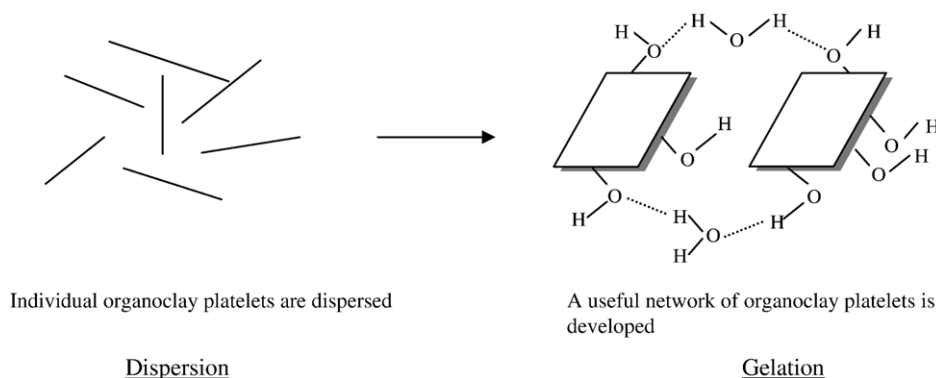


Fig. 1. Dispersion and gelation mechanisms.

(alcohols, ketones, amides, nitriles) and mechanical shear. The gel structure of the grease is caused by hydrogen bonding between dispersed organoclay particles creating a gel network (Fig. 1).

This mechanism requires additional compounds capable of hydrogen bond formation, such as water to achieve maximum gelation (Kieke et al., 1988).

In continuity with our studies on the properties and possible uses of Tunisian natural products (Chtourou et al., 2004), this research was conducted to validate the usefulness of two Tunisian bentonites as thickening agents in high performance lubricating greases formulations.

## 2. Experimental procedures

### 2.1. Chemicals

Two bentonites (noted B<sub>1</sub> and B<sub>2</sub>) selected from the south of Tunisia were used. They have, after purification and Na<sup>+</sup> exchange with 1M NaCl solution, cation exchange capacities (CEC) of 75.6 and 99.6 meq 100 g<sup>-1</sup>. The surface properties of these clays were modified with two quaternary ammonium salts (Aldrich Chemicals): hexadecyl benzyl dimethylammonium chloride (HBDMA) and dioctadecyl dimethylammonium chloride (DODMA).

A mineral based lubricating oil was used. Some physicochemical characteristics were measured independently by SOTULUB (Bizerte–Tunisia) (Table 1).

### 2.2. Modification of the bentonites

The purified and Na<sup>+</sup> exchanged bentonites were dispersed at 2% (in mass) in a mixture (90v/10v) of water and ethanol. The dispersion was then placed in a reactor equipped with a vapour condenser, and was gradually heated to 80 °C, under mechanical agitation.

When this temperature remained constant, the quaternary ammonium salt (QAS) solution was added to the dispersion and the reaction was carried out for 3 h. The QAS concentration was equivalent to 100% of the CEC of the Na<sup>+</sup>-purified bentonites. Presence of ethanol facilitated the solubilization of ammonium salts. Resulting organoclays noted DODMA-B<sub>1</sub>, DODMA-B<sub>2</sub>, HBDMA-B<sub>1</sub> and HBDMA-B<sub>2</sub>, were recovered by filtration, washed several times by distilled water and finally dried at 85±5 °C. The physicochemical and rheological properties of the prepared organoclays had been studied in a previous work (Chtourou et al., 2005).

### 2.3. Semi quantitative X-ray diffraction analysis

The XRD patterns were obtained with an X'Pert Pro PANalytical diffractometer operating at 40 kV and 40 mA using Cu- $\alpha_1$  radiation. Diffraction patterns were recorded on oriented films of organoclays and Na<sup>+</sup>-bentonites between 2° and 30° (2 $\theta$ ) at a step size of 0.017°. Diffraction patterns of the Na<sup>+</sup>-bentonites were recorded before and after glycolization.

The semi-quantitative mineralogical composition of the Na<sup>+</sup>-bentonites (noted B<sub>1p</sub> and B<sub>2p</sub>) was determined by X-ray diffraction (Holtzapfel, 1985). The X-ray

Table 1  
Physicochemical characteristics<sup>a</sup> of mineral oil used

Test	ASTM <sup>b</sup> method	Mineral oil
Carbon residue (%)	ASTM D-189	0.20
Pour point (°C)	ASTM D-2500	-1
Flash point (°C)	ASTM D-92	246
Viscosity at 40 °C (cSt)	ASTM D-445	109–116
Viscosity index <sup>c</sup>	ASTM D-2270	90

<sup>a</sup> Mean of two replicates. Standard deviations (SD) were 7–10%.

<sup>b</sup> ASTM: American Standards for Testing and Materials.

<sup>c</sup> Viscosity index: It is a number that indicates the effect of temperature changes on the viscosity of the oil.

Table 2  
Compositions of produced greases

Constituent	Mass percentage				
	Grease 1	Grease 2	Grease 3	Grease 4	Grease 5
Thickener %	BDMH-B <sub>1</sub> 11.0	DMDO-B <sub>1</sub> 11.0	BDMH-B <sub>2</sub> 10.0	DMDO-B <sub>2</sub> 11.0	Bentone 34 10.0
Lubricating oil	84.0	84.0	85.0	84.0	85.0
Additives:					
Antioxidants	2.0	2.0	2.0	2.0	2.0
Adhesiveness	1.5	1.5	1.5	1.5	1.5
Rust inhibitors	1.0	1.0	1.0	1.0	1.0
EP agents	0.5	0.5	0.5	0.5	0.5

patterns were treated by the WinPLOTR program to fit the peaks and eliminate the background noise. The obtained corrected intensities ( $I_{\text{corr}}$ ) were then multiplied by the following corrective factors ( $\alpha$ ): 1.25 for smectite, 1.0 for illite and 0.7 for kaolinite (Holtzapf, 1985). The percentage of each mineral was calculated with the following formula: % mineral ( $i$ ) =  $\frac{I_{\text{corr}}(i) \times \alpha(i)}{\sum_j I_{\text{corr}}(j) \times \alpha(j)}$ .

#### 2.4. Preparation of lubricating greases

The organoclays were dispersed in a portion of the lubricating oil (50% of the total amount) in the presence of an amount of acetone, equal to 10% by weight of organoclay. Dispersion was accomplished by mechanical shear in a rotor stator mill under a rotation speed of 5000 rpm. The resulting pregel was then heated to remove acetone and the remaining amount of oil was added, under agitation, to adjust the final composition.

After cooling, specific additives were added to the product to improve some of its intrinsic properties (Jolicœur, 1992). Among these additives, we used antioxidant agents, rust inhibitors, adhesiveness agents and extreme-pressure (EP) agents. Greases were finally homogenized by milling with a rotor–stator homogeniser. The compositions of the produced greases are given in Table 2.

### 3. Results and discussion

#### 3.1. Mineralogical composition of the purified bentonites

The X-ray diffraction patterns of the  $\leq 2\text{-}\mu\text{m}$  clay fraction of the bentonites B<sub>1p</sub> and B<sub>2p</sub> are presented in Fig. 2. The 001 reflection of B<sub>2p</sub> ( $d_{001} = 12.6 \text{ \AA}$ ) was the characteristic of a sodium smectite or an interstratified sample of this mineral with illite. The basal spacing of B<sub>1p</sub> ( $d_{001} = 14.7 \text{ \AA}$ ) was larger than that of B<sub>2p</sub>, but could as well correspond to a sodium smectite. The

difference between these  $d_{001}$  may be a result of the control of the humidity during X-ray data collection (Xi et al., 2004).

Treatment with ethylene glycol shifted the 001 reflection to  $17.1 \text{ \AA}$ , and thus confirmed the presence of smectite or interstratified smectite–illite. The position of the 002 reflections is very sensitive to smectite–illite interstratification (Srasra and Trabelsi-Ayedi, 2001). It varies from  $8.46 \text{ \AA}$  for a pure smectite to  $10.0 \text{ \AA}$  for a pure illite. Our glycolated samples (Fig. 3) showed that the 002 reflections appeared at  $9.48 \text{ \AA}$  for B<sub>1p</sub> and at  $9.76 \text{ \AA}$  for B<sub>2p</sub> thus indicating the irregular interstratification of these clays.

The semi-quantitative mineralogical composition (Table 3) showed that the smectite fraction was higher in clay B<sub>2p</sub> than that in clay B<sub>1p</sub>. This result was in agreement with the values of the CEC of the purified clays, when we consider that the CEC was due to the smectite fraction.

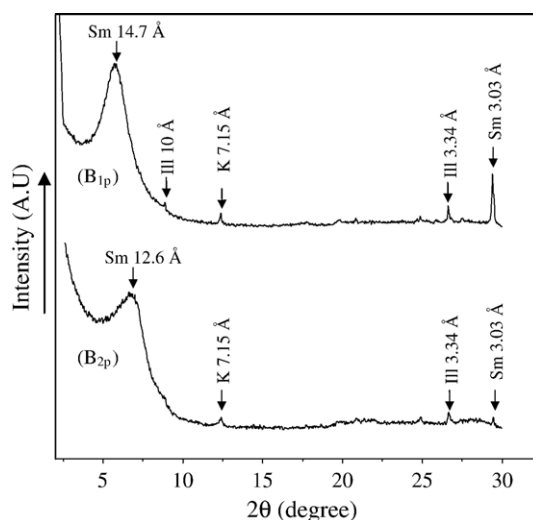


Fig. 2. X-Ray diffraction patterns on oriented films of the Na<sup>+</sup>-bentonites. (Sm: Smectite, Ill: Illite, K: Kaolinite).

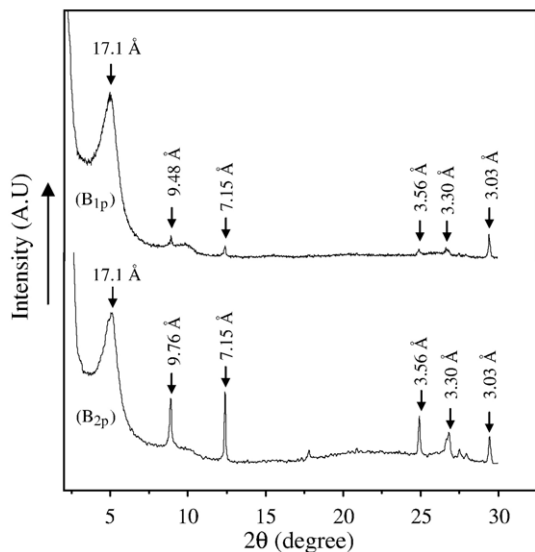


Fig. 3. X-Ray diffraction patterns on oriented films of the glycolated  $\text{Na}^+$ -bentonites.

### 3.2. Structure of the prepared organoclays

The basal spacing ( $d_{001}$ ) of the  $\text{Na}^+$ -bentonites was increased by organic modification due to the intercalation of the organic molecules (Lagaly, 1986).

According to the model of Lagaly and Weiss (Yilmaz and Yapar, 2004), the increase of the basal spacing (Fig 4) corresponded to a bilayer arrangement of surfactant molecules in the interlayer space of HBDMA- $\text{B}_2$  and DODMA- $\text{B}_2$  and a random interstratification of monolayer and bilayer structures for HBDMA- $\text{B}_1$  and DODMA- $\text{B}_1$  (Le Pluart, 2002; Halvaty and Fajnor, 2002; Yilmaz and Yapar, 2004).

Previous works, using a surfactant concentrations equal to 100% of the CEC, have found  $d_{001}=19.72 \text{ \AA}$  for octadecyl trimethylammonium bentonite (Xi et al., 2004) and  $d_{001}=18.41 \text{ \AA}$  for hexadecyl trimethylammonium bentonite (Yilmaz and Yapar, 2004). The basal spacing of DODMA- $\text{B}_1$  and DODMA- $\text{B}_2$  and of HBDMA- $\text{B}_1$  and HBDMA- $\text{B}_2$  chain were in agreement with these results.

The basal spacing of DODMA- $\text{B}_1$  (19.46  $\text{\AA}$ ) and DODMA- $\text{B}_2$  (19.83  $\text{\AA}$ ) were higher than those of HBDMA- $\text{B}_1$  (18.96  $\text{\AA}$ ) and HBDMA- $\text{B}_2$  (18.62  $\text{\AA}$ ).

Table 3  
Mineralogical composition ( $\pm 2\%$ ) of the  $\leq 2\text{-}\mu\text{m}$  clay fraction

Sample	Smectite	Illite	Kaolinite
$\text{B}_{1p}$	85	11	4
$\text{B}_{2p}$	91	6	3

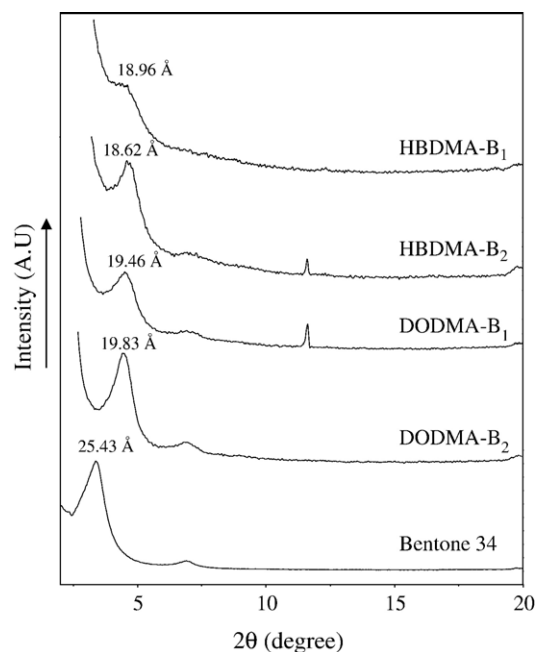


Fig. 4. X-Ray diffraction patterns on oriented films of organoclays.

This result was due to the difference in the chain length of the intercalated surfactant cations.

The organoclay of reference (Bentone 34) presented high basal spacing, which can be attributed to a pseudotrimolecular layer structure and may be a result of a surfactant concentration higher than 100% of the CEC (Xi et al., 2004).

### 3.3. Characterization of the finished greases

Physicochemical and mechanical testing methods were realized on the finished greases to evaluate their performance. The results of the tests applied to the greases were grouped in Table 4.

Lubricating greases are considered to be plastic solids, hence the measurement of their consistency is desirable. To determine the consistency of lubricating greases (ASTM D-217, 1995), a penetrometer measured, in tenths of a millimeter, the depth to which the standard cone penetrated the grease. The sample of grease was subjected to 60 double strokes with a mechanical grease worker, a machine designed to operate the plunger of the grease worker mechanically. This apparatus was essential for the measurement of a prolonged worked penetration (100 000 double strokes).

The unworked penetrations (UnW.P) do not generally represent the consistency of the greases in use as effectively as the worked penetrations (W.P) do. The values of UnW.P varied from one grease to another (from

Table 4  
Characteristics of finished greases<sup>a</sup>

TEST	Grease 1	Grease 2	Grease 3	Grease 4	Grease 5	EP grease specifications <sup>b</sup>
Unworked penetration <sup>c</sup> , UnW.P (10 <sup>-1</sup> mm)	326	322	321	318	244	–
Worked penetration 60 strokes <sup>c</sup> , W.P (10 <sup>-1</sup> mm)	332	332	327	328	242	–
NLGI consistency number	1	1	1	1	3	0 to 3
Worked penetration 100,000 strokes <sup>c</sup> , W.P (10 <sup>-1</sup> mm)	330	342	340	350	310	–
$\Delta_2 = \text{W.P}_{100000} - \text{W.P}_{60}$ (10 <sup>-1</sup> mm)	-2	+10	+13	+32	+68	$\leq +45.0$
$\Delta$ : Shell roller test <sup>c</sup> , 2 h at 25 °C (10 <sup>-1</sup> mm)	+35.7	+45.5	+48.7	+58.5	+32.5	$\leq +45.0$
Oil separation <sup>c</sup> , 42 h at 40 °C (%)	6.6	4.8	4.2	4.3	1.3	5.0 max
Dropping point <sup>c</sup> (°C)	168	155	199	203	216	185 min
Copper corrosion, 24 h at 100 °C (color)	1b	1b	1b	1b	1b	1a
Wheel bearing test <sup>c</sup> , 6 h at 105 °C (g)	5.5	7.7	5.5	6.0	2.0	10.0 max
Four-ball test <sup>c</sup> , weld (kgf)	230	230	230	230	250	200 min

<sup>a</sup> For compositions of these greases see Table 2.

<sup>b</sup> Sotulub (Bizerte, Tunisia) specifications for extreme-pressure greases.

<sup>c</sup> Mean data of two replicates. Standard deviations (SD) were 7–10%.

244 10<sup>-1</sup> mm for grease 5 to 326 10<sup>-1</sup> mm for grease 1). This variation was related to the nature and the structure of the organoclay used as a thickening agent.

The UnW.P values depend on the strength of the gel structure of the grease. There exists a negative correlation between the UnW.P values and the  $d_{001}$  of the organoclays, as shown in Table 5.

The higher the values of  $d_{001}$  are, the better the consistency of the grease is. Indeed, a necessary condition of gel formation in organic media is the intracrystalline swelling and dispersing of organoclays in the given medium (Moraru, 2001). The  $d_{001}$  of the organoclay strongly depends on the CEC of the clay and the size of the intercalated organic cation. The thickening capability of the organoclay and the strength of the gel structure depend on the size of the interlayer organic cations (Moraru, 2001), thus they increase with the rise of the basal  $d$ -spacing.

W.P results may be used to establish the consistency of lubricating greases within the NLGI (National Lubricating Grease Institute) consistency numbers shown in Table 6 (ASTM D-217, 1995).

The values of worked penetration after 60 strokes (W.P<sub>60</sub>) showed that greases 1, 2, 3, 4 and 5 had NLGI numbers of 1, 1, 1, 1 and 3, respectively. Greases of NLGI number 1 are recommended for use in manual or automatic lubricating systems. They have better mobility and are the preferred choice for colder applications,

automatic lubrication systems with long pumping runs and other applications.

The changes in UnW.P results of a grease after working of 60 strokes ( $\Delta_1 = \text{W.P}_{60} - \text{UnW.P}$ ), and in W.P results after a prolonged working of 100 000 strokes ( $\Delta_2 = \text{W.P}_{100\,000} - \text{W.P}_{60}$ ) were believed to be a measure of its shear stability. The change in W.P of grease after rolling in shell roller test ( $\Delta$ ) was believed to be a measure of its mechanical stability at rolling. The lower the values of  $\Delta_1$ ,  $\Delta_2$  and  $\Delta$  are, the better the mechanical stability is.

Grease 5 ( $\Delta_1 = -2.0 \cdot 10^{-1}$  mm), taken as reference, had better stability to the mechanical working of 60 strokes than grease 1 ( $\Delta_1 = +6.0 \cdot 10^{-1}$  mm), grease 2 ( $\Delta_1 = +10.0 \cdot 10^{-1}$  mm), grease 3 ( $\Delta_1 = +6.0 \cdot 10^{-1}$  mm) and grease 4 ( $\Delta_1 = +10.0 \cdot 10^{-1}$  mm). Although greases specifications do not give a limiting value for  $\Delta_1$ , the obtained results were comparable to those of previous works (Magauran, 1987; Kieke et al., 1988) regarding their greases as having good mechanical stability to working.

The values of  $\Delta_2$  (Table 4) showed that greases 1, 2, 3, and 4 had good shear stability when subjected to the mechanical influence of 100 000 strokes, since all these values were  $\leq +45$  (limiting value tolerated for EP greases). The produced greases present better stability to prolonged working than the grease 5 ( $\Delta_2 = +68.0 \cdot 10^{-1}$  mm).

In the shell Roller test (ASTM D-1831, 1995), the grease was laminated between two rollers at 25 °C

Table 5  
UnW.P Values and the  $d_{001}$  of the corresponded organoclays

	Grease 1	Grease 2	Grease 3	Grease 4	Grease 5
UnW.P (10 <sup>-1</sup> mm)	326	322	321	318	244
Organoclay	HBDMA-B <sub>1</sub>	DODMA-B <sub>1</sub>	HBDMA-B <sub>2</sub>	DODMA-B <sub>2</sub>	Bentone 34
$d_{001}$ of the organoclay (Å)	18.96	19.46	18.62	19.83	25.43

Table 6  
NLGI<sup>a</sup> consistency numbers of lubricating greases

NLGI consistency number	Worked penetration range, 25 °C (mm × 10)
000	445–475
00	400–430
0	355–385
1	310–340
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

<sup>a</sup> NLGI, National Lubricating Grease Institute.

during 2 h. The penetration ( $P$ ) was then measured and compared to the worked penetration after 60 double strokes. The result of the test was expressed by  $\Delta = P -$  worked penetration (60 strokes).

Greases **1**, **2** and **5** had good mechanical stability at rolling since the values found in shell roller test (Table 4) were  $\leq +45$  (limiting value tolerated for EP greases). Grease **1** ( $\Delta = +35.7 \cdot 10^{-1}$  mm) had stability comparable to that of the reference grease **5** ( $\Delta = +32.5 \cdot 10^{-1}$  mm).

The test of oil separation (ASTM D-1742, 1995) documents the tendency of lubricating grease to de-homogenise during storage. The values found in this test showed that greases **1**, **2**, **3** and **4** gave percentages of oil separation higher than that of the reference grease **5**, but, with the exception of grease **1**, less than 5%, in conformity with the EP greases specifications. A grease specification is a detailed description of the features and the performance characteristics to which the grease must conform. The homogeneity of the lubricating grease was related to its consistency. For this reason, grease **1** gave the higher percentage of oil separation. In deed, grease **1** was less consistent than the other greases since its UnW. P value was the higher (Table 4).

The dropping point was the temperature at which grease passed from its semisolid state to its fluid state. The measurement of the dropping point (ASTM D-2265, 1995) determined generally the thermal stability of grease. Greases **3** and **4** had dropping points comparable to grease **5** and in conformity with the EP grease specifications (Table 4). We noted better thermal performance of greases **3** and **4**, formulated with B<sub>2p</sub>. They had, respectively, dropping points of 199 and 203 °C better than those of grease **1** (168 °C) and grease **2** (155 °C) formulated with B<sub>1p</sub>. It seems that the mineralogical composition and the CEC of the starting bentonite had a great influence on the thermal stability of the resulting grease. In deed, B<sub>2p</sub> presented a higher smectitic fraction than B<sub>1p</sub> (Table 3). It seems that this

difference can affect the thermal stability of the resulting grease. On the other, B<sub>2p</sub> had a CEC higher than B<sub>1p</sub>. The amount of surfactants adsorbed by HBDMA-B<sub>2</sub> and DODMA-B<sub>2</sub> was therefore higher than by HBDMA-B<sub>1</sub> and DODMA-B<sub>1</sub>. Therefore, greases **3** and **4**, thickened by HBDMA-B<sub>2</sub> and DODMA-B<sub>2</sub>, needed higher temperatures to fluidify than greases **1** and **2**, thickened by HBDMA-B<sub>1</sub> and DODMA-B<sub>1</sub>.

The test of copper strip corrosion (ASTM D-130, 1995) made it possible to evaluate the corrosivity of lubricating greases with respect to the copper parts or copper alloys. The results found in this test (Table 4) showed that greases **1**, **2**, **3**, **4** and **5** did not corrode the copper parts, since the results approached that of the ASTM strip no. 1 (ASTM D-130, 1995), with a dark orange color (1b). These results were expected since the same percentages of rust inhibitor and antioxidant additives were used for all the prepared greases. In deed, lubricating greases do not have intrinsic anticorrosion properties; it is the addition of rust inhibitor and antioxidant additives that gave them these properties.

The wheel bearing test (ASTM D-1263, 1999) covers the evaluation of the leakage tendencies of wheel bearing greases. Leakage of grease or oil, or both, was measured. Low values (in g) on this test indicate better resistance of the grease to leakage.

Results obtained for greases **1**, **2**, **3** and **4** (Table 4) were higher than that obtained for the grease **5**, taken as reference. However, these results were less than 10 g, in conformity with the extreme-pressure greases specifications.

The four-ball test (ASTM D-2596, 1997) was indispensable to evaluate the extreme-pressure (EP) properties of the greases. Higher values (in Kgf) of the weld point indicate better stability of the grease to high-load conditions.

Greases **1**, **2**, **3** and **4** had weld point comparable to that of the reference grease **5** and greater than 200 Kgf, in conformity with the EP greases specifications (Table 4). The values of the weld point of greases **1**, **2**, **3** and **4** (containing 0.5% EP additives) were significantly higher than those obtained by M. Kieke (Kieke et al., 1988) for organoclay based greases using 1.0% EP additives. Due to these good EP properties, the greases produced provide outstanding protection for four wheel drive steering knuckles, spring shackles, and heavy equipment pivot joints.

#### 4. Conclusion

The lubricating greases prepared from Tunisian bentonites had properties comparable to those of the

commercial (Bentone 34) grease and in conformity with the extreme-pressure greases specifications. They presented a good mechanical stability to working, to prolonged working and to rolling. They also presented good performances in corrosion, oil separation and wheel bearing tests. The obtained greases had good EP properties with only 0.5% EP additives. In light of these results, we could consider using these bentonites in the preparation of high performance lubricating greases.

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