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1 **Enhancing the rheological properties and thermal stability of**  
2 **oil-based drilling fluids by synergetic use of organo-**  
3 **montmorillonite and organo-sepiolite**

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23 Abstract

24 This work focused on improving the rheological properties and thermal stability  
25 of oil-based drilling fluids by using the mixture of organo-montmorillonite (OMt) and  
26 organo-sepiolite (OSep) as the rheological additive. OMt and OSep were prepared in  
27 water. X-ray diffraction (XRD), scanning electron microscope and transmission  
28 electron microscope were applied to characterize the structure of organoclays (OC).  
29 The OC/oil gels were characterized using an appropriate XRD method. Dynamic  
30 rheological test was used to appraise the rheological behavior, viscosity, gel strength  
31 and thixotropy of OC/oil fluids aged at different temperatures. OMt firstly swelled in  
32 oil at low temperature, and then exfoliated above 150°C. OSep maintained its crystal  
33 structure all the time. The mixing of these two OC did not obviously influence their  
34 structures. However, the gel formation ability was promoted, resulting in improvement  
35 of rheological properties and thermal stability of oil-based drilling fluids. The  
36 nanolayers of OMt and nanofibers of OSep interweaved with each other, reinforcing  
37 the network structure and protected them from collapse at high temperatures. The  
38 mixture of OMt and OSep with mass proportion of 50% for each displayed the optimal  
39 rheological properties and thermal ability.

40

41 **Keywords:** Sepiolite, oil-based muds, rheological properties, organic modification,  
42 high temperature.

43

44

## 45 1. Introduction

46 Over the next 30 years, global energy is projected to rise almost 60%, a  
47 challenging trend that may be met only by revolutionary breakthroughs in energy  
48 science and technology (Esmaeili, 2011). Although the technologies of some new or  
49 renewable energies (such as new battery, wind energy, nuclear energy, etc.) are  
50 developing fast, oil and gas, as the traditional energy, are the main energy resource in  
51 the world. The demand of oil and gas is increasing due to the rapid development of the  
52 society. However, the petroleum industry is increasingly drilling more technically  
53 challenging and difficult wells. Drilling of deeper wells worldwide requires constants  
54 searching for adequate drilling fluids to overcome extreme conditions (Williams et al.,  
55 2011).

56 Drilling fluids are compared as “the bloods of drilling operations”. By drilling  
57 operations, oil and gas can be extracted from the earth. Drilling fluids serve several  
58 fundamental functions, such as (i) to remove the cuttings generated by the drill bit from  
59 the borehole, (ii) to control the downhole formation pressures, (iii) to overcome the  
60 fluid pressure of the formation, (iv) to avoid damage to the producing formation and (v)  
61 to cool and lubricate the drill bit, etc. (Chilingarian and Vorabutr, 1983; Caenn and  
62 Chillingar, 1996; Meng et al., 2012). Generally, drilling fluids can be divided into two  
63 types based on the continuous phase, i.e., water-based drilling fluids and oil-based  
64 drilling fluids. Water-based drilling fluids are limited by their abilities of dissolving  
65 salts, interfering with the flow of oil and gas through porous rocks, promoting the  
66 disintegration and dispersion of clay minerals, and effecting the corrosion of iron

67 (Caenn et al., 2011). Oil-based drilling fluids, owing to their excellent lubricity, high  
68 rate of penetration, shale inhibition, wellbore stability, high lubricity, high thermal  
69 stability (Caenn and Chillingar, 1996; Khodja et al., 2010), are advised to be used to  
70 drill difficult wells. In spite of the advantages of oil-based drilling fluids, drilling  
71 practice always demand drilling fluids with greater rheological properties and better  
72 thermal stability.

73 Organoclays (OC) are used in oil-based drilling fluids to control the rheological  
74 behavior. They perform specific functions in a base oil and are varied in amount to  
75 furnish the properties required for satisfying the conditions of use. Organo-  
76 montmorillonite (OMt) is mostly used in oil-based drilling fluids (Caenn et al., 2011;  
77 Dino and Thompson, 2013; Zhuang et al., 2016, 2017b). Hermoso et al. (2014) reported  
78 that the viscous flow behavior of oil-based drilling fluids is deeply influenced by OMt  
79 nature and concentration. (Schmidt, 1987) proposed that OC did not viscosify the oils  
80 but built the structure through interactions with the aqueous phase (water phase is usually  
81 included in oil-based drilling fluids). But later work (Burgentzle et al., 2004)  
82 demonstrated that OMt can viscosify organic solvents without water. Previous work  
83 (Zhuang et al., 2017b, d) reported the exfoliation of OMt in oil aged at high  
84 temperatures. Exfoliated OMt produced many nanolayers to build a “house of cards”  
85 structure, resulting in the improvement of gel formation and rheological properties. By  
86 comparing studies on different modifiers, surfactants containing two long alkyl chains  
87 was proved to be easier to result in exfoliation of OMt in oil and excellent rheological  
88 properties. However, distinct decline of the rheological properties occurred when best

89 fluids aged above 180°C, because of two potential ways, i.e., thermal decomposition  
90 and desorption of organic surfactants.

91 Recently, the OC from palygorskite-sepiolite family were reported to be used in oil-  
92 based drilling fluids (Dino and Thompson, 2002; Zhuang et al., 2017a, c, d, 2018b;  
93 Weng et al., 2018). They exhibited excellent rheological properties in oil by forming a  
94 “haystack” structure. These clay minerals are natural nanofibrous materials. For  
95 sepiolite (Sep), its fiber sizes generally range from 0.2 μm to 2 μm in length, 100 nm to  
96 300 nm in width and 50 nm to 100 nm in thickness (Alvarez, 1984; Álvarez et al., 2011).  
97 Accordingly, Sep shows preeminent rheological properties in polar solvents. By organic  
98 modification, organo-sepiolite (OSep) displays the lipophilicity and can perform  
99 excellent rheological properties in oil (Zhuang et al., 2018a).

100 Some recent literature reported about the joint use of Mt and fibrous clay minerals  
101 (Neaman and Singer, 2000; Chemedá et al., 2014; Al-Malki et al., 2016) to enhance the  
102 rheological properties of clay minerals in solvents. Al-Malki et al. (2016) found that  
103 bentonite-based drilling mud with Sep nanoparticles showed a great stability in plastic  
104 viscosity and yield point over a wide range of temperature and pressure, especially at  
105 high temperatures and pressures. The previous work enlightened that synergistic use of  
106 OMt and OSep may also promote the rheological properties and thermal stability of oil-  
107 based drilling fluids. This is a promising way to sustain oil-based drilling fluids work  
108 in difficult wells.

109 Aiming to improve the rheological properties and thermal stability of oil-based  
110 drilling fluids, OMt and OSep was synergistically used in oil-based fluids aged at

111 different temperatures and their structures and rheological properties were  
112 characterized.

113

## 114 2. Materials and Methods

### 115 2.1 Materials

116  $\text{Na}^+$ -treated Mt was obtained from Kazuo, Liaoning, China, with the purity of ca.  
117 84% and cation exchange capacity (CEC) of 120 cmol/kg. Sep was obtained from Spain,  
118 with the CEC of 35 cmol/kg. The purity of clay minerals was defined X-Ray diffraction  
119 method according to the Chinese standard SY/T 5163-2010. Details of this method were  
120 reported in previous literature (Zhuang et al., 2018a). Some quartz (12%), calcite (4%)  
121 and albite (2%) were included in the Mt sample (see Fig. 1 (A)). XRD pattern of Sep  
122 (Fig. 1 (B)) matches well with the JCPDS card of Sep and no other reflections are  
123 observed, indicating the high purity of Sep. The chemical composition of Mt and Sep  
124 were characterized by X-ray fluorescence (XRF) analysis and the results are listed in  
125 Table 1. Both of these two clay minerals were milled and sieved with a 200-mesh sieve  
126 before use. Benzyl dimethyl octadecyl ammonium chloride (C18, purity of 97%) and  
127 dimethyl dioctadecyl ammonium chloride (DC18, purity of 98%) were bought from  
128 Anhui Super Chemical Technology Co., Ltd, China. The white oil (No. 5) was bought  
129 from China National Petroleum Corporation.

130

### 131 2.2 Preparation of OC

132 OMt was prepared in aqueous solution as the following steps: 100 g of Mt was

133 added into 1 L deionized water, stirring for 0.5 h; then DC18 (1.0 CEC of Mt) was  
134 added into the previous dispersion, stirring for 1 h; at last, by centrifugation, drying at  
135 60°C for 24 h, milling and sieving with a 200-mesh sieve. OSep was prepared as the  
136 following steps: C18 (35% of the mass of Sep) was firstly dissolved into 500 mL  
137 distilled water (keep at 60°C in the whole process), 100 g of Sep was added into the  
138 previous solution, stirred for 1 h and thickened slurry was obtained; at last, after drying  
139 at 60°C for 24 h, milling and sieving with a 200-mesh sieve, OSep was prepared.

### 140 2.3 Preparation of Sep/oil fluids

141 12 g of OC was added into 400 mL white oil (concentration of 30 kg/m<sup>3</sup>) and  
142 blended at 10000 rpm for 20 min. A drilling fluid should be aged at different  
143 temperatures to model the real drilling operation. According to the standards of API  
144 SPEC 13A and API RP 13B-2, the resulting fluid was placed in a rotary oven heated to  
145 66°C, 150°C, 180°C and 200°C where it was aged for 16 h. The mixtures of OC in oil-  
146 based drilling fluids are listed in Table 2. The corresponding fluid is named as OC/oil-  
147 temperature. For example, the oil-based fluid of OMT<sub>0.5</sub>-OSep<sub>0.5</sub> and oil aged at 150°C  
148 is named as OMT<sub>0.5</sub>-OSep<sub>0.5</sub>/oil-150.

149

### 150 2.4 Characterization

151 The X-ray diffraction (XRD) analysis was conducted on a Bruker D8 Advance X-  
152 ray powder diffractometer operating at Cu K $\alpha$  radiation, 40 kV, 40 mA and a scan speed  
153 of 0.05 s per step (step size: 0.02°). The XRD patterns were collected from 3° to 70°.  
154 Particularly, the XRD test for OC/oil gels is described in the section 3.1. Scanning



155 electron microscope (SEM) images were obtained with a HITACHI SU8000 type SEM  
156 and the operating voltage was 10 kV. The transmission electron microscope (TEM)  
157 analysis was conducted on a JEM 1200EX TEM equipment and operated at the voltage  
158 of 200 kV. Gel volume results were obtained by adding 100 mL aged fluid into a  
159 graduated cylinder with a stopper and standing for 24 h. The dynamic rheological  
160 behavior of oil-based fluids was tested by a Thermo Scientific HAAKE Roto Visco 1  
161 rotational viscometer at 20°C. The tested program was: the shear rate linearly increased  
162 from 0 s<sup>-1</sup> to 100 s<sup>-1</sup> in 5 min (up step), and then linearly decreased from 100 s<sup>-1</sup> to 0 s<sup>-1</sup>  
163 in 5 min (down step).

164

### 165 3. Results and discussion

#### 166 3.1 XRD analysis

167 The XRD patterns of Mt and OMt were presented in Fig. 1 (A). There were some  
168 impurities, i.e., quartz and calcite in the Mt sample. The basal reflection of Mt occurred  
169 at  $2\theta = 7.05^\circ$ , with the basal spacing of 1.25 nm. Modified with DC18, a group of  
170 reflections emerged at  $2.40^\circ$ ,  $4.82^\circ$  and  $7.34^\circ$ , which were attributed to the reflections  
171 of (001), (002) and (003) crystalline planes. The basal spacing of OMt increased to 3.68  
172 nm, indicating the successful intercalation of DC18 into the interlayer space. In Fig. 1  
173 (B), the XRD pattern of OSep is nearly the same with that of Sep. This phenomenon  
174 demonstrated that the organic modification could not influence the crystal structure of  
175 Sep, similar with the modification of palygorskite (Zhuang et al., 2017a, c). This is  
176 because that the TOT (T refers [SiO<sub>4</sub>] tetrahedron and O refers to [Al(Mg)O<sub>6</sub>]

177 octahedron) layers were linked by covalent bonds. Based on the TGA results (see Fig.  
178 S1, in supplementary materials), there were 40.8% and 23.4% of organic surfactants  
179 included in OMT and OSep, respectively.

180 The OC/oil gels were also characterized by XRD using an appropriate method (see  
181 Fig. 2 (A)). Firstly, the OC/oil fluid was dripped on oil-absorbing papers. After 24 h of  
182 natural absorption, extra oil was removed and the OC/oil gel was obtained. OC/oil gels  
183 were marked following the template of “OC/oil-temperature”. Finally, the OC/oil gels  
184 can be tested using the X-ray diffractometer similar with powder samples. The XRD  
185 patterns of sample holder and sample holder with oil are shown in Fig. 2 (B). The  
186 sample holder exhibited a small reflection with low intensity. However, a wider  
187 reflection occurred in the XRD pattern of sample holder + oil, with higher intensity.  
188 These two reflections are typical amorphous ones, in agreement with the previous  
189 literature (Ribotta et al., 2004; Bates et al., 2006; Ford et al., 2010; Rowe and Brewer,  
190 2017). Thus, this reflection between 8 to 30° and centering at ca. 17° is assigned to the  
191 amorphous reflection of oil.

192 The XRD patterns of OC/oil gels aged at different temperatures are presented in Fig.  
193 3. A wide reflection in the range of  $2\theta = 8-30^\circ$  emerged in the XRD patterns of OC/oil  
194 gels, centering at 17 to 18°. They are attributed to the oil as proved in Fig. 2 (B). These  
195 wide reflections demonstrated that oil molecules were packaged in the network  
196 structures of OC. The intensity of these reflections can be used to evaluate the oil  
197 contents in the gels. Compared with OMT, the XRD patterns of OMT/oil-66 and OMT<sub>0.8</sub>-  
198 OSep<sub>0.2</sub>/oil-66 showed that the basal spacing of OMT in these two gels increased to 5.04

199 nm: indeed, oil molecules are probably in the interlayer space due to the lipophilicity.  
200 In the XRD pattern of OMt<sub>0.5</sub>-OSep<sub>0.5</sub>/oil-66, both intensities of reflections attributed  
201 to OMt and OSep dramatically reduced, indicating disordered arrangements parallel to  
202 the c-axis of OMt and the b-axis of OSep. When the mass content of OSep increased to  
203 80%, the basal reflection of OMt disappeared in the XRD pattern of OMt<sub>0.2</sub>-  
204 OSep<sub>0.8</sub>/oil-66. Considering the changes in the XRD patterns of OMt<sub>0.5</sub>-OSep<sub>0.5</sub>/oil-66  
205 and OMt<sub>0.2</sub>-OSep<sub>0.8</sub>/oil-66, the mixing of OMt and OSep facilitated the exfoliation of  
206 OMt. The XRD pattern of OSep/oil-66 is similar with that of OSep powder, in spite of  
207 the wide reflection from 8° to 30°.

208 With the temperature rising, the wide reflection of oil showed high intensity,  
209 indicating more oil molecules contained in the gel structures. This fact proved that high  
210 temperatures promoted the formation of a stronger network structure with large  
211 interspace. OSep/oil gels maintained the reflections of Sep at different temperatures.  
212 However, the basal reflections of OMt/oil gels aged above 150°C disappeared, probably  
213 suggesting the exfoliation of OMt. But the (100) reflection, which emerged at  $2\theta =$   
214  $19.7^\circ$ , was kept in the XRD patterns of OMt/oil gels. This phenomenon implied that the  
215 individual TOT structures were kept and changes just happened to the arrangement  
216 paralleling to the c-axis. The basal reflection of OMt was not observed in the mixture  
217 of OMt and OSep aged at high temperatures, indicating the exfoliation of OMt. With  
218 the increase of OSep, OC/oil gels exhibited higher intensity of the (110) reflection,  
219 because of the more proportion of OSep. Significantly, the XRD patterns of these  
220 OC/oil aged from 150°C to 200°C showed the similar reflections, indicating that they

221 kept the structures in this temperature range.

222

### 223 3.2 SEM and TEM

224 The SEM and TEM images are presented in Fig. 4. OMt is associated with a large  
225 number of silicate layers. To some extent, these layers are soft so that they may be  
226 curved. Based on the TEM image of OMt, the lamellae contain at least 10 layers. The  
227 distance between two adjacent layers was measured as 3.56 nm. This value is a little  
228 smaller than the basal spacing derived from the XRD result. This is because the high  
229 voltage of TEM test (200 kV) would destroy the interlayer surfactants and/or  
230 dehydration of the interlayer space (Kogure, 2013). Hence, the basal spacing calculated  
231 from the TEM depended on the voltage, test time, thermal stability of organic  
232 compounds and the thickness of samples. The exfoliation of OMt was defined as no  
233 further interaction occurs between the two delaminated units (isolated layers or stacking  
234 of few layers) which become independently mobile in the liquid phase (Bergaya et al.,  
235 2012), so that the no long-range order was apparent along the c-axis. The exfoliated  
236 OMt layers would form a “house of cards” structure by surface to edge and edge to  
237 edge arrangements.

238 The SEM and TEM images of OSep showed the disordered aggregation of OSep  
239 fibers. The length of fibers ranged from hundreds of nanometers to ca. 1  $\mu\text{m}$ . Indeed,  
240 the OSep existed in the forms of individual fibers (rods), laths and bundles (García-  
241 Romero and Suárez, 2013). The crystal laths and bundles, which consist of nanofibers,  
242 are very hard to be disaggregated, due to the electronic attraction, Van der Waals forces

243 and hydrogen bonding interaction (Haden and Schwint, 1967; Xu et al., 2014). The  
244 aggregation of different forms of OSep built a “haystack” structure (Haden, 1963).

245 The SEM or TEM images of OC/oil gels can't be obtained, because of the high  
246 amount of oil present in the gels. Indeed, it is difficult to remove the oil because of its  
247 high boiling point and non-volatile ability.

248

### 249 3.3 Gel volume

250 The gel volume results (see Fig. 5) can directly show the gel formation ability and  
251 compatibility between oil and OC. At the initial time ( $t = 0$  s), all the gel volumes of  
252 OC/oil fluids were set as 100.0 mL. When the time went to 90 min, the gel volumes of  
253 OMT, OMT<sub>0.8</sub>-OSep<sub>0.2</sub>, OMT<sub>0.5</sub>-OSep<sub>0.5</sub>, OMT<sub>0.2</sub>-OSep<sub>0.8</sub> and OSep in oil were 21.8 mL,  
254 97.2 mL, 98.0 mL, 100.0 mL and 100.0 mL, respectively. After standing four 24 h, the  
255 gel volumes became 15.7 mL for OMT, 67.1 mL for OMT<sub>0.8</sub>-OSep<sub>0.2</sub>, 89.5 mL for  
256 OMT<sub>0.5</sub>-OSep<sub>0.5</sub>, 100.0 mL for OMT<sub>0.2</sub>-OSep<sub>0.8</sub> and 100.0 mL for OSep. OMT showed  
257 the least gel volume in oil while OSep presented the gel volume of 100.0 mL. At room  
258 temperature, OMT can only absorb a part of oil molecules, resulting in the expanding of  
259 interlayer space. The swelling OMT particles dispersed and stacked in oil, without  
260 prominent contributions to promoting the network structure and gel formation.  
261 However, TEM images testified that OSep is in the form of fibers, laths and bundles,  
262 which are in nanoscale. These fibers laths and bundles could be easier to form “haystack”  
263 structures, leading to the high and stable gel volumes. The gel volumes of OMT/OSep  
264 mixture in oil increased with the increase of OSep proportion. This phenomenon

265 suggested that the addition of OSep contributed to the gel formation of OMt in oil.

266

### 267 3.4 Rheological properties

268 The dynamic rheological curves of OC/oil fluids are presented in Fig. 6. These  
269 curves display the rheological behavior and thermal stability of corresponding OC/oil  
270 fluids. Aged at 66°C, OMt/oil fluid showed the highest shear stress, indicating that  
271 OMt/oil fluid displayed the best viscosity. OMt/oil and OSep/oil fluids aged at 66°C  
272 showed the different curves of up step and down step. However, in the rheological  
273 curves of the mixture of OMt and OSep fluids, the down step curves nearly followed  
274 the up step curves. This fact demonstrated that the network structures of OMt and  
275 OSep in oil obviously changed while no distinct structural changes happened in the  
276 mixture fluids. The single OC built their own network structures in oil. But the new  
277 network structure didn't form well in the mixed oil fluids aged at 66°C. In addition,  
278 the rheological curves of fluids aged at 66°C followed the Bingham plastic model at  
279 10-100 s<sup>-1</sup>, except for OSep/oil aged at 66°C.

280 When the temperature increased to above 150°C, the rheological curves became  
281 very different. Firstly, the shear stresses of fluids aged above 150°C is much larger  
282 than those of fluids aged at 66°C, demonstrating the promotion of network structures  
283 and viscosity by high temperatures. Furthermore, in the up step, a rapid climb was  
284 observed before 20 s<sup>-1</sup>, and then a dramatical decline occurred. Consequently, there  
285 was a critical point which showed the highest shear stress. This critical point  
286 suggested that a large shear stress must be applied to break the connected aggregates

287 of OC and to disperse and orient stacked nanoplatelets or nanofibers (maybe nano  
288 laths and bundles) in the flow direction (Zhuang et al., 2017b). In the down step, the  
289 curves were nearly lines (in spite of the derivation at 0-20 s<sup>-1</sup>), in agreement with the  
290 Bingham plastic model. No critical points were seen in the down step because the  
291 network had been sheared at high shear rate and the network structures were  
292 destroyed.

293 These critical points can indicate the gel strengths of network structures. The  
294 shear stress results corresponding to these critical points are listed in Table 3. Aged at  
295 66°C, OSep/oil fluid showed a little different rheological curve from other fluids, due  
296 to the changes at 0-40 s<sup>-1</sup> in up step. It was a critical range, instead of a point, because  
297 the network structure was not enough strong. The critical shear stresses of OMt/oil  
298 and OSep/oil fluids firstly increased and then decreased, indicating that the increase  
299 of aging temperature firstly improved the formation of network structure and higher  
300 temperature would be harmful for the network structure, due to the thermal  
301 degradation and/or desorption of organic surfactants. The critical shear stress of  
302 OMt<sub>0.8</sub>-OSep<sub>0.2</sub>/oil fluid gradually decreased with the temperature rising. However,  
303 OMt<sub>0.5</sub>-OSep<sub>0.5</sub>/oil and OMt<sub>0.2</sub>-OSep<sub>0.8</sub>/oil fluids showed basically stable critical  
304 shear stresses from 150°C to 180°C, and little higher ones at 200°C. This  
305 phenomenon demonstrated the better stability of the mixture of OMt and OSep than  
306 single OC in oil-based drilling fluids.

307 The shear stresses of samples at 100 s<sup>-1</sup> were applied to evaluate the viscosities ( $\eta$ )  
308 of different fluids (Table 4). As  $\eta = \tau/\gamma$  and  $\gamma$  was constant ( $\tau$  refers to shear stress and

309  $\gamma$  refers to shear rate), i.e.,  $100 \text{ s}^{-1}$ ,  $\tau$  can be used to indicate the changes of  $\eta$ . Aged at  
310  $66^\circ\text{C}$ , the  $\tau$  values of samples were very low, because the OC were not exfoliated  
311 completely or dispersed well. With the temperature rising, the  $\tau$  values dramatically  
312 increased due to the fine formation of network structures which was promoted by high  
313 temperatures. For example, the  $\tau_{66-150}$  values of OMt/oil, OMt<sub>0.8</sub>-OSep<sub>0.2</sub>/oil, OMt<sub>0.5</sub>-  
314 OSep<sub>0.5</sub>/oil, OMt<sub>0.2</sub>-OSep<sub>0.8</sub>/oil and OSep/oil were 108%, 378%, 687%, 696% and  
315 694%. Compared with the  $\tau$  values at  $180^\circ\text{C}$ , OMt/oil, OMt<sub>0.8</sub>-OSep<sub>0.2</sub>/oil and OSep/oil  
316 at  $200^\circ\text{C}$  decreased by 49%, 26% and 18%. However, the  $\tau$  values of OMt<sub>0.5</sub>-OSep<sub>0.5</sub>  
317 and OMt<sub>0.2</sub>-OSep<sub>0.8</sub> at  $200^\circ\text{C}$  increased by 46% and 18%. These results also supported  
318 that the mixture of OMt and OSep benefited the viscosity and thermal stability of oil-  
319 base drilling fluids.

320 Thixotropy represents a reversible isothermal transformation of a colloidal sol to  
321 a gel. It is caused by the clay mineral units slowly arranging themselves in positions of  
322 minimum free energy. In drilling practice, low resistance (low viscosity) is expected for  
323 the bit to ensure high drilling rate, while high viscosity is expected for carrying cuttings.  
324 Excellent thixotropy of an oil-based drilling fluid is necessary. The areas of thixotropic  
325 loops (abbreviated as A, see in Table 5) in Fig. 6 are applied to evaluate the thixotropy  
326 of OSep/oil fluids.

327 Aged at  $66^\circ\text{C}$ , the A value of OMt/oil fluid was  $22.5 \text{ Pa}\cdot\text{s}^{-1}$  and that of OSep/oil  
328 fluid was  $39.38 \text{ Pa}\cdot\text{s}^{-1}$ . The A values of OMt<sub>0.8</sub>-OSep<sub>0.2</sub>/oil, OMt<sub>0.5</sub>-OSep<sub>0.5</sub>/oil and  
329 OMt<sub>0.2</sub>-OSep<sub>0.8</sub>/oil fluids ranged from 2.39 to  $4.82 \text{ Pa}\cdot\text{s}^{-1}$ , indicating nearly no  
330 thixotropy of these samples. High temperatures promoted the gel formation. The A



331 values of samples increased until aged at 180°C, except for those of OMt<sub>0.5</sub>-OSep<sub>0.5</sub>/oil  
332 and OMt<sub>0.2</sub>-OSep<sub>0.8</sub>/oil. The decrease rates of OMt/oil, OMt<sub>0.8</sub>-OSep<sub>0.2</sub>/oil and  
333 OSep/oil from 180°C to 200°C ( $A_{180-200}$ ) were 71%, 49% and 24%. OMt/oil declined  
334 more than OSep/oil. OMt<sub>0.5</sub>-OSep<sub>0.5</sub>/oil and OMt<sub>0.2</sub>-OSep<sub>0.8</sub>/oil exhibited continuous  
335 and slow augment of the A values until to 200°C, so that these two samples can be  
336 basically regarded as stable samples. The A values of OMt<sub>0.5</sub>-OSep<sub>0.5</sub>/oil and OMt<sub>0.2</sub>-  
337 OSep<sub>0.8</sub>/oil at 150-200°C were much more than those of a single OC, demonstrating  
338 that the mixture of OMt and OSep contributed to improving the thixotropy of oil-based  
339 fluids.

340       Considering all the discussions of rheological properties, the mixture of OMt and  
341 OSep, with the mass proportion of 50% for each, can effectively improve the viscosity,  
342 gel strength, thixotropy and thermal stability of the oil-based fluids.

343

### 344 3.5 Network structure

345       The rheological test proved that the OMt<sub>0.5</sub>-OSep<sub>0.5</sub> performed greater rheological  
346 properties and better thermal stability in oil than each single OC did. This enhancement  
347 was resulted by the mixed network structure (see Fig. 7). When mixing OMt and OSep  
348 in oil, they firstly disperse following their own nature. At low temperature, oil  
349 molecules were adsorbed into the interlayer space of OMt, resulting in swelling. OMt  
350 was mostly in the form of swelled particles, perhaps with a little exfoliated nanolayers.  
351 OSep fibers, laths and crystal bundles dispersed in oil. Although the mass proportions  
352 of these two OC were identical, the number of OMt particles was much less than the

353 number of OSep fibers, laths and bundles. Due to the difference of these numbers, OMt  
354 and OSep had no strong contact with each other. But the mixing of these two OC still  
355 improved their gel formation in oil (see Fig. 5).

356 As the XRD results demonstrated that OMt exfoliated in oil above 150°C, one OMt  
357 particle might divided into dozens or hundreds of nanolayers. Consequently, the number  
358 of OMt layers dramatically increased. Influenced by the thermal motion, these  
359 nanolayers mixed and contact with the nanofibers, laths and bundles. Significantly, the  
360 “house of cards” structure of OMt and the “haystack” structure were not independent.  
361 These two different shapes of silicate units (layered OMt and fibrous OSep)  
362 interweaved with each other, leading to a stronger network structure. Previous work  
363 testified that organic surfactants would decomposed or/and dissolved into oil at high  
364 temperature, resulting the shrink of OMt (Zhuang et al. 2017b). In this mixed network  
365 structure, exfoliated OMt layers were supported by OSep fibers, and the OSep fibers  
366 were also sustained by the nanolayers.

367

#### 368 4. Conclusion

369 In summary, synergetic use of OMt and OSep can improve the rheological  
370 properties and thermal stability of oil-based drilling fluids. OMt firstly swelled in oil  
371 by adsorbing oil molecules while OSep showed stable dispersion due to its nanoscale  
372 fibers, laths and bundles. At high temperature, thermal motion promoted the exfoliation  
373 of OMt into nanolayers. The interweave of nanofibers (laths and bundles) of nanolayers  
374 enhanced the network structure, resulting in improvement of rheological properties.

375 The mutual support between OMT nanolayers and OSEP nanofibers protected this  
376 network structure from crush at high temperatures.

377

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383

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## Figures

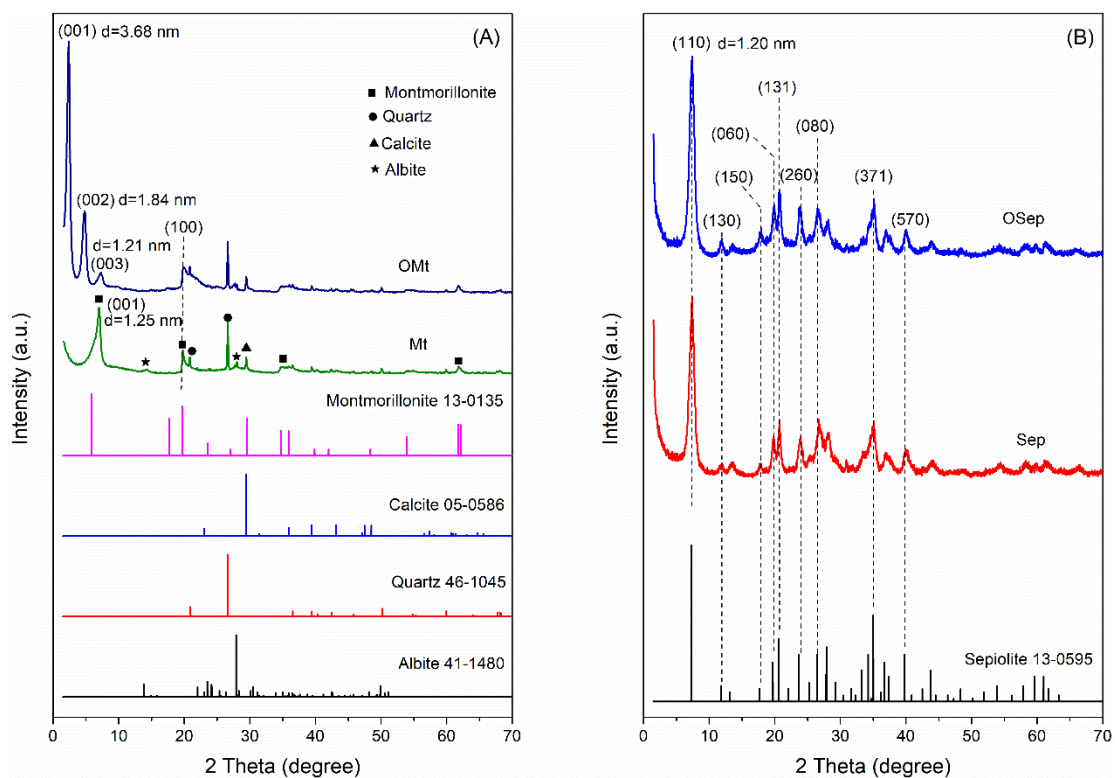


Fig. 1 XRD patterns of (A) Mt, OMT, (B) Sep and OSep.

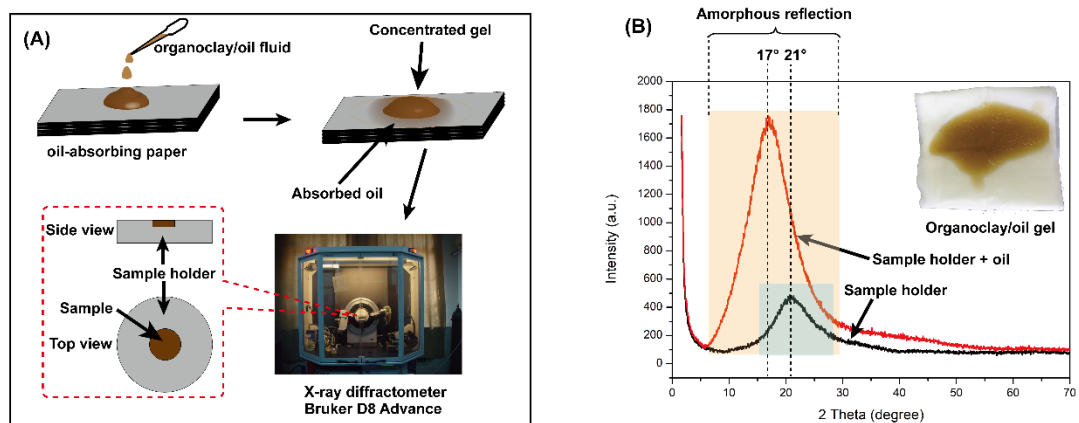


Fig. 2 (A) Interpretive diagram of XRD test for OC/oil gel sample and (B) XRD patterns of the sample holder and sample holder with oil.



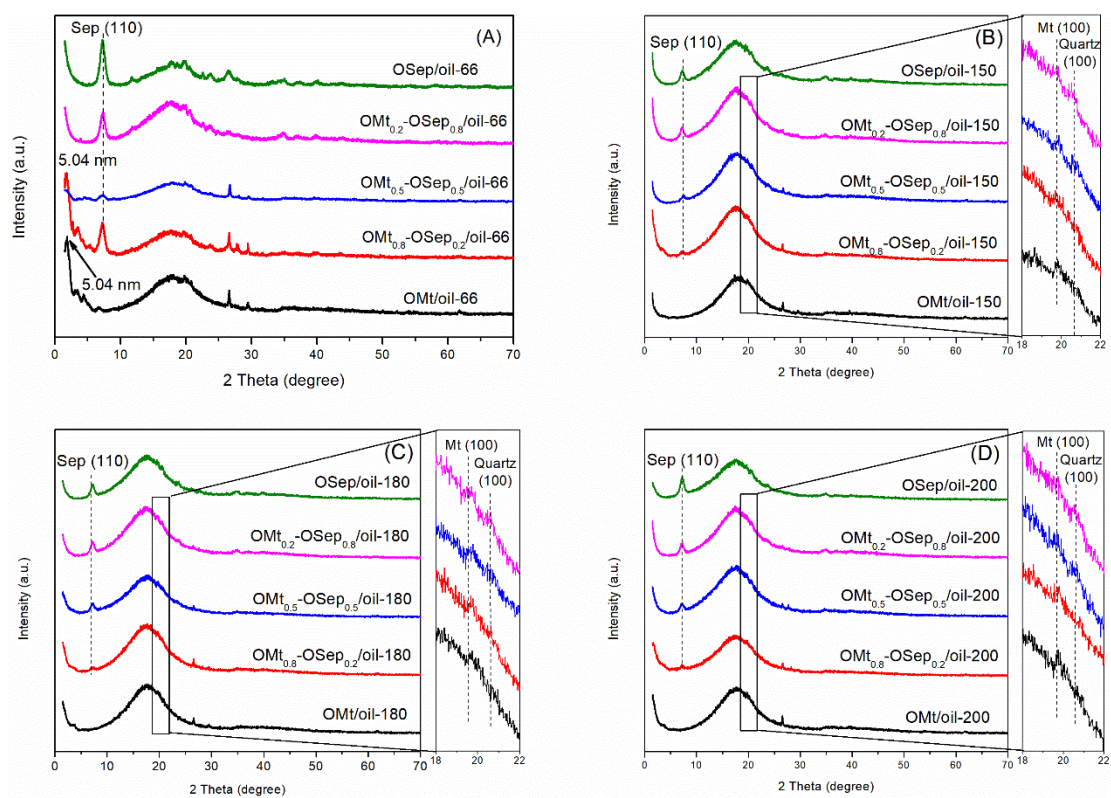


Fig. 3 XRD patterns of OC/oil gels aged at (A) 66°C, (B) 150°C, (C) 180°C and 200°C.

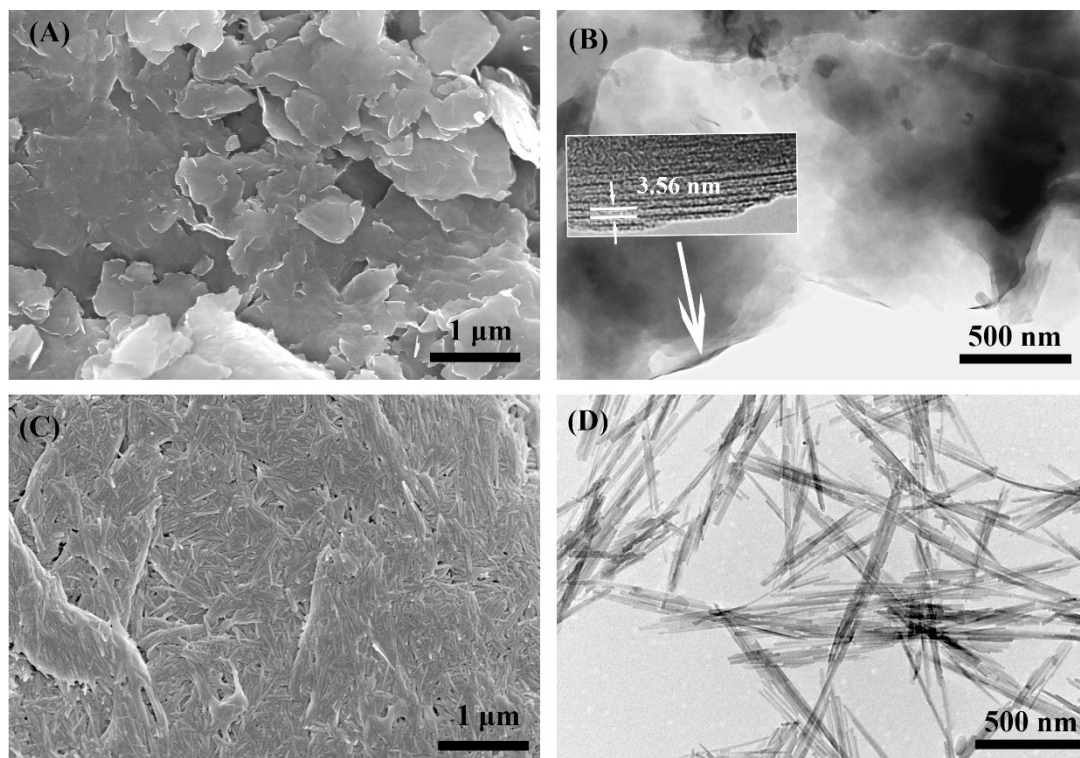


Fig. 4 SEM images of (A) OMT and (C) OSep; TEM images of (B) OMT and (D) OSep.

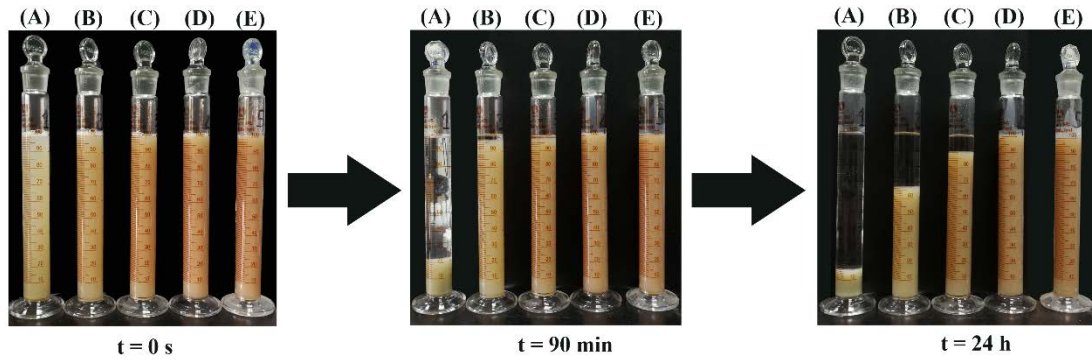


Fig. 5 Gel volume results of (A) OMT, (B) OMT<sub>0.8</sub>-OSep<sub>0.2</sub>, (C) OMT<sub>0.5</sub>-OSep<sub>0.5</sub>, (D) OMT<sub>0.2</sub>-OSep<sub>0.8</sub> and (E) OSep in oil.

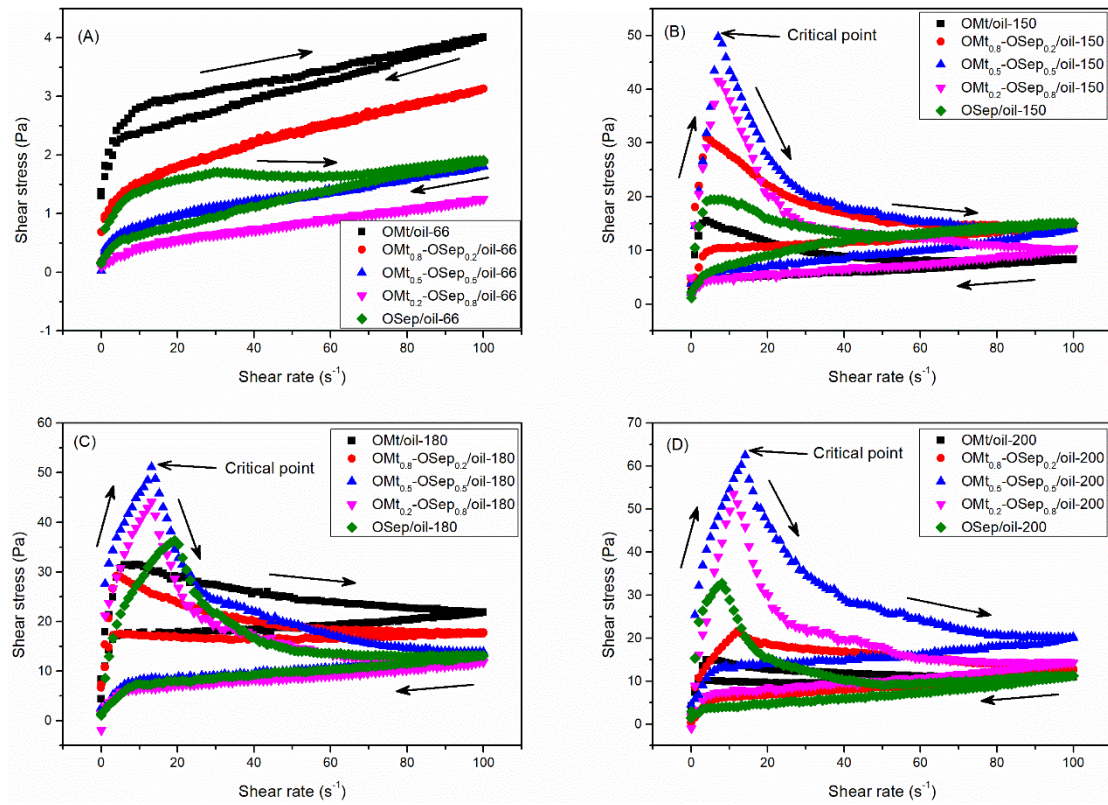


Fig. 6 Dynamic rheological curves of OC/oil fluids aged at (A) 66°C, (B) 150°C, (C) 180°C and (D) 200°C for 16 h.

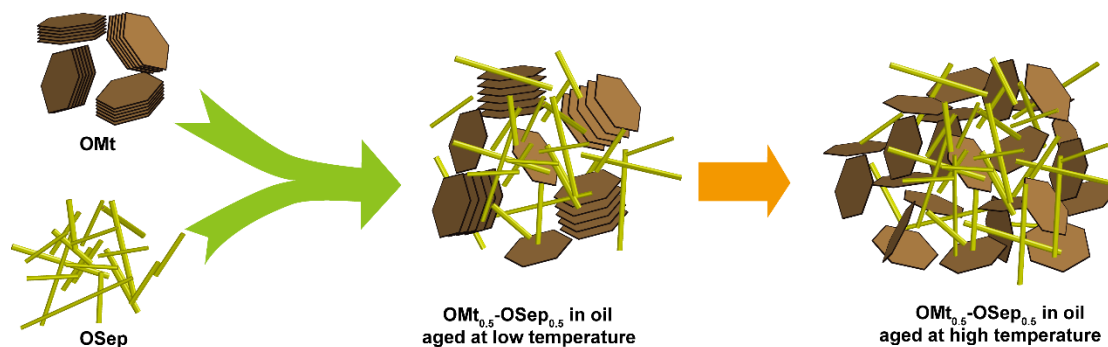


Fig. 7 the Interpretive diagram of the network structure of the mixed OMT and OSEP in oil.

Figure captions:

Fig. 1 XRD patterns of (A) Mt, OMT, (B) Sep and OSEP.

Fig. 2 (A) Interpretive diagram of XRD test for OC/oil gel sample and (B) XRD patterns of the sample holder and sample holder with oil.

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Tables

Table 1 Chemical composition of Mt and Sep (derived from XRF results)

Sample	Composition (mass %)						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	others
Mt	64.40	19.71	4.16	3.75	3.72	3.30	0.96
Sep	63.68	9.88	1.26	19.41	0.87	3.35	1.55

Table 2 Details of the mixtures of OMt and OSep.

Sample	OMt (mass %)	OSep (mass %)
OMt	100	0
OMt <sub>0.8</sub> -OSep <sub>0.2</sub>	80	20
OMt <sub>0.5</sub> -OSep <sub>0.5</sub>	50	50
OMt <sub>0.2</sub> -OSep <sub>0.8</sub>	20	80
OSep	0	100

Table 3 A summary of shear stress results corresponding to the critical points.

Sample	Shear stress (Pa)			
	66°C	150°C	180°C	200°C
OMt/oil	none	15.62	31.41	15.28
OMt <sub>0.8</sub> -OSep <sub>0.2</sub> /oil	none	31.50	29.33	22.05
OMt <sub>0.5</sub> -OSep <sub>0.5</sub> /oil	none	50.12	51.08	62.67
OMt <sub>0.2</sub> -OSep <sub>0.8</sub> /oil	none	41.52	44.49	53.81
OSep/oil	none	19.64	36.53	33.06

Table 4 A summary of shear stress ( $\tau$ ) at the shear rate ( $\dot{\gamma}$ ) of 100 s<sup>-1</sup>.

Sample	$\tau$ (Pa)				$\tau_{66-150}$ (%)	$\tau_{180-200}$ (%)
	66°C	150°C	180°C	200°C		
OMt/oil	4.02	8.36	21.53	10.96	108	-49
OMt <sub>0.8</sub> -OSep <sub>0.2</sub> /oil	3.13	14.95	17.60	13.10	378	-26
OMt <sub>0.5</sub> -OSep <sub>0.5</sub> /oil	1.80	14.16	13.96	20.34	687	46
OMt <sub>0.2</sub> -OSep <sub>0.8</sub> /oil	1.25	9.95	11.78	13.86	696	18
OSep/oil	1.91	15.16	13.29	10.85	694	-18

Note:  $\tau_{66-150} = (\tau_{150} - \tau_{66}) / \tau_{66} \times 100\%$ , similarly,  $\tau_{180-200} = (\tau_{200} - \tau_{180}) / \tau_{180} \times 100\%$ ;  $\tau_x$

refers to the shear stress at 100 s<sup>-1</sup> of fluids aged x°C.

Table 5 The areas of thixotropic loops (A) in Fig. 6.

Sample	A (Pa·s <sup>-1</sup> )				A <sub>66-150</sub>	A <sub>180-</sub>
	66°C	150°C	180°C	200°C	(%)	200
						(%)
OMt/oil	22.50	325.97	635.20	186.22	1349	-71
OMt <sub>0.8</sub> -OSep <sub>0.2</sub> /oil	3.46	600.86	710.46	361.12	17266	-49
OMt <sub>0.5</sub> -OSep <sub>0.5</sub> /oil	4.82	1097.75	1281.62	1497.10	22675	17
OMt <sub>0.2</sub> -OSep <sub>0.8</sub> /oil	2.39	907.37	1011.93	1080.78	37865	7
OSep/oil	39.38	275.34	842.99	644.85	599	-24

Note:  $A_{66-150} = (A_{150} - A_{66}) / A_{66} \times 100\%$ , similarly,  $A_{180-200} = (A_{200} - A_{180}) / A_{180} \times 100\%$ ;

A<sub>x</sub> refers to the area of a sample aged at x°C.