PETROLEUM AND GAS PROCESSING

CARBONATION STAGE IN SYNTHESIS OF ADDITIVE "MASK"

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The additive MASK (high-alkalinity calcium alkylsalicylate) is classed among the so-called overbased additives [1]. The information available in the literature on the structure of such additives is quite extensive but very contradictory. In our opinion, the most correct view is that of Schilling, Smalher, Dodgeson, et al. [2-4] that overbased additives are colloidal dispersions of metal oxides or hydroxides in the hydrocarbon part of the additive. Grounds for this opinion are (in particular) the Tyndall effect manifested by oil solutions of such additives and the fact that the number of metal atoms per molecule of additive is often greater than could be expected for any known type of complex, as distinguished from a pure compound.

The synthesis of such dispersions is usually performed by a carbonation method. As applied to the MASK additive, it consists of treating ASK additive (calcium alkylsalicylate with 20-25% excess alkalinity) with calcium hydroxide and then passing carbon dioxide through the mixture in the presence of a promoter. The calcium carbonate that is formed remains in the product in the form of a colloidal dispersion. The properties of such an additive depend largely on the stability of the system that is formed and also on the amount of excess alkalinity. However, current views differ on the optimal upper limit for the alkalinity of the MASK additive. Great difficulties also arise in producing an additive with the required degree of purity. A number of studies [5-8] have been devoted to the problem of how to obtain pure additives. However, most of these investigators have considered only the question of how to clean up the finished additives. Successful removal of solid contaminants depends not only on proper selection of treating conditions, but also on the quantity and nature of the insoluble materials that have been formed, and this in turn is closely related to the conditions of synthesis. The solid contaminants that are formed during carbonation consists mainly of undispersed particles of the metal carbonate, along with excess metal hydroxide. Hence, the carbonation process should be conducted in such a manner that a minimal amount of excess hydroxide is used in producing a stable colloidal dispersion.

Difficulties are being encountered in the commercial production of MASK additive, and these difficulties cannot be overcome until we obtain a better understanding of the carbonation process. Hence we have undertaken a study of how the process parameters influence the additive properties and how we can define conditions such that the additive produced will have the required physicochemical and service characteristics.

We have studied the influence of the amount of water, the concentration of promoter (methanol), calcium hydroxide content, and temperature, on the course of the carbonation process. The techniques that were developed for this work provided for the measurement of the amount of carbon dioxide consumed in the formation of dispersed calcium carbonate. The carbon dioxide feed rate was controlled by the rate of absorption in the reaction. The calcium hydroxide charged to the reactor was uniformly distributed throughout the reaction volume, and mixing conditions were identical in all experiments. These considerations are particularly important because the process is heterogeneous.

Water in amounts from 0 to 30% by weight was added to the ASK additive to determine the effect on additive properties. In all experiments, a 2-h reaction period was sufficient for reaction of the calculated amount of carbon dioxide consumed in the formation of dispersed calcium carbonate. The carbon dioxide feed rate was controlled by the rate of absorption in the reaction. The calcium hydroxide charged to the reactor was uniformly distributed throughout the reaction volume, and mixing conditions were identical in all experiments. These considerations are particularly important because the process is heterogeneous.

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TABLE 1. Physicochemical and Service Properties of MASK Additive at Various Levels of Excess Alkalinity

<table>
<thead>
<tr>
<th>Total alkalinity, mg/KOH/g</th>
<th>Excess alkalinity, % stoichiometric</th>
<th>Contamination level, mg/100 g</th>
<th>Viscosity at 100°C, cSt</th>
<th>Thermal-oxidative stability, min</th>
<th>Corrosivity, g/cm²</th>
<th>Oxidation in DK-2 apparatus</th>
<th>Hot-plate coking of DS-16 oil with 25% MASK additive</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sludge, %</td>
</tr>
<tr>
<td>123.9</td>
<td>220</td>
<td>100</td>
<td>16.8</td>
<td>80</td>
<td>3.3</td>
<td>None</td>
<td>14.1</td>
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<tr>
<td>198.5</td>
<td>400</td>
<td>200</td>
<td>50.5</td>
<td>85</td>
<td>None</td>
<td>None</td>
<td>14.1</td>
</tr>
<tr>
<td>265.8</td>
<td>600</td>
<td>1200</td>
<td>149.8</td>
<td>90</td>
<td>None</td>
<td>None</td>
<td>17.1</td>
</tr>
</tbody>
</table>

*Solution of additive in paphtha centrifuged 10 min in a laboratory centrifuge with a separation factor of 900 g.

Fig. 1. Change in excess alkalinity of product during carbonation with various amounts of added water: 1) No water; 2) 13.3% water on ASK additive; 3) 30% water on ASK additive.

Fig. 2. Increase in calcium carbonate content of additive as a function of quantity of reacted CO₂, with different amounts of added promoter (methanol): 1) 0.9 mole of methanol per mole of calcium hydroxide; 2) 1.2 and 1.5 moles of methanol per mole of calcium hydroxide; 3) theoretically calculated increase in calcium hydroxide; 3) theoretically calculated increase in calcium carbonate content of additive.

of the experiment (Fig. 1, curve 1). In the experiments in which water was added, the alkalinity increased and reached a maximum before the entire calculated quantity of carbon dioxide had reacted, after which the alkalinity decreased (see Fig. 1, curves 2 and 3), the drop in alkalinity being greater for the experiments in which the greater amount of water was added. A drop in alkalinity was also observed after the calculated quantity of carbon dioxide had reacted.

When the carbonation was performed with added water, it was found that at the moment of completing the process, i.e., when the entire calculated quantity of CO₂ had reacted, the quantity of dispersed calcium carbonate amounted to about 40—60%, depending on the amount of added water. This means that only about half of the calcium hydroxide charge was used to impart alkalinity to the additive, the remainder precipitating in the form of solid contaminants. When the carbonation was performed without added water, the degree of calcium hydroxide utilization was more than 80%.

The influence of water on this process can be explained as follows. During the carbonation, the formation of calcium carbonate particles is accompanied by growth of these particles to sizes at which they can no longer be dispersed by the additive. When water is added, the process of calcium carbonate particle growth is at first far slower than the process of forming these particles. Then the growth rate becomes much faster. This leads to a drop in the excess alkalinity. Under these circumstances, it is difficult to carry out the commercial synthesis of ad-