Study on Over-Based Sulfurized Calcium Phenate Homologs (Part 1)*

—Structure, Composition and Physical Properties of Mixed Homologs in Oil-Diluent—

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Summary: Eighteen samples of over-based sulfurized calcium phenates containing from about 150 to 1,000% of the theoretical amount of calcium were prepared from *p*-octylphenol, calcium oxide, elemental sulfur, ethylene glycol, carbon dioxide, lauryl alcohol and oil used as starting materials, and their structure, composition and physical properties were studied.

From the ebullioscopic results, the active ingredients of these over-based phenates proved to be amphipathic substances having a polymer structure. Based on the material balance, it was revealed that these ingredients consisted of four ligand components (*p*-octylphenol, sulfur, ethylene glycol and carbon dioxide) and calcium, and there existed among their components continuous quantitative relationships, e.g. a decrease, in a hyperbolic manner, in the molar ratio of the total ligands to calcium in the products with an increase in the blending-molar ratio of calcium to *p*-octylphenol.

In conclusion, these over-based phenates seem to be oil solutions of mixed homologs of an amphipathic coordination-condensation polymer homologous series.

1 Introduction

For a clear understanding of the behavior of over-based phenates in lubricating oils, an accurate knowledge of their structure and composition is of great value. Although these phenates are in common use and various preparation methods are known today, unfortunately, only a limited amount of fundamental work has been reported on these phenates, and very little exact knowledge is available concerning their structure and composition.

In this work, eighteen samples of 1.5 to 10.0 BEQ phenates all of which possessing satisfactory oil soluble characteristics were prepared by the method¹⁾ using *p*-octylphenol (POP), elementary sulfur (S), calcium oxide (CaO), ethylene glycol (EG), carbon dioxide (CO₂), lauryl alcohol (LA) and diluent oil (OIL) as starting materials, and their structure, composition and physical properties were studied. In the above, BEQ means the number of equivalents of CaO blended per equivalent of POP.

For the over-based phenates, hitherto, various

structures were postulated^{2b)}, but only the one, suggested by Smalheer and Mastin³⁾, Stewart and Stuart^{2b)} in which phenate molecules adsorb colloidal particles of metal oxide, hydroxide or carbonate present in excess of the stoichiometric amount in the normal phenate, appears to be generally accepted. However the above suggested structure has not been proved.

Therefore, the first object of this work is to isolate a relatively stable 2.0 BEQ active ingredient as a representative sample of this series, then to confirm ebullioscopically whether it has the same structure as that suggested by Smalheer et al. or not.

The second object is to confirm by study of the composition as to which starting materials are incorporated into the active ingredients and in what proportion. Although ethylene glycol, as well as both lauryl alcohol and oil, has been known as a solvent^{2a)}, in the process for preparing various phenates, some doubt arises as to whether EG functions only as a solvent.

The third object is to find out any regularity among the compositions in a series of products obtained by using the same starting materials under similar conditions, and to investigate any relation between the regularity and physical pro-

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perties.

2 Experimental

2.1 Materials

p-Octylphenol of 97.5 wt% purity was used without further purification. The main impurities found by gas chromatography were butylphenol (1.3 wt%) and phenol (0.3 wt%). Calcium oxide of 98 wt% purity used was obtained from a lime of industrial special grade (JIS-R-9001) of 94.6 wt% purity by heating it at 800 °C after removal of the impurities with a 200 mesh wire gauge. Lauryl alcohol used as a solvent was of commercial grade whose composition by gas chromatography consisted of: *n*-dodecyl alcohol (96.9 wt%), *n*-decyl alcohol (0.2 wt%) and *n*-tetradecyl alcohol (2.9 wt%). Ethylene glycol used was of chemical pure grade. Carbon dioxide used was of 99.5 wt% purity in a cylinder. Elementary sulfur used was of 99.8 wt% purity (JIS-M-8513). Diluent Oil used was a highly solvent-refined light paraffinic lubricating oil having viscosities of 4.07 cS at 210°F and 21.4 cS at 100°F, a viscosity index of 97, a flash point of 200 °C by Cleveland Open Cup method, and a specific gravity (15/4 °C) of 0.859.

2.2 Preparation of Samples

Samples of over-based sulfurized calcium phenates were prepared by the procedure modified from the method previously described¹⁾.

The blending ratios of raw materials for preparing eighteen samples having different (1.5~10.0) BEQ are shown in **Table 1**. The detailed procedure for preparing 1.5 BEQ product (No. 1), presented as a typical example, was carried

out as follows.

To a suspension containing 309.5 g of POP, 64.1 g of CaO, 62.6 g of S and 742.7 g of LA, 125.8 g of EG was added in a nitrogen atmosphere at 135 °C, and the mixture was stirred at the same temperature for 5.5 hours (5.5 hours in the cases of No. 1, 2, 3 and 4; 6.0 hours in the cases of No. 5, 6, 7, 8, 9 and 10; 7.0 hours in the cases of No. 11, 12, 13, 14, 15, 16, 17 and 18), while removing the hydrogen sulfide generated, to give 1,288.2 g of dark yellowish red solution (I).

From 1,283.5 g of this solution, water, unreacted EG and a small amount of LA were distilled off in a nitrogen atmosphere under reduced pressure to give 1,056.1 g of a dark yellowish red residue (II). The final distillation temperature was 128°C under 9 mmHg.

Into 1,048.4 g of the distillation residue, CO₂ was introduced at 110 to 127 °C under pressure (up to 11 kg/cm²) to effect absorption, and the mixture was kept at 165°C (165°C in the cases of No. 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10; 145°C in the cases of No. 11, 12, 13, 14, 15, 16, 17 and 18) for additional two hours to give 1,084.7 g of a dark yellowish red CO₂-treated mixture (III).

To 1,068.5 g of the mixture, 212.7 g of OIL was added, and the resulting mixture was distilled in a nitrogen atmosphere under reduced pressure to remove a small amount of EG, a major portion of LA, and a small portion of OIL to give 561.0 g of a dark yellowish red residual material (IV). The final distillation temperature under 3 mmHg was 223°C.

From this residual material, 1.4 g of *n*-hexane insolubles was removed, and finally 559.1 g of

Table 1 Blending Ratio of Starting Materials

Run No.	BEQ	[CaO]/[POP] (mol/mol)	[EG]/[CaO] (mol/mol)	[S]/[POP] (g-atom/mol)	[LA]/[POP] (wt/wt)	[OIL]/[POP] (wt/wt)
1	1.5	0.75	1.8	1.3	2.4	0.70
2	2.0	1.00	"	"	2.5	1.00
3	2.2	1.10	"	"	2.6	1.18
4	2.4	1.20	"	"	2.7	1.30
5	2.6	1.30	"	"	2.8	1.38
6	2.8	1.40	"	"	2.9	1.46
7	3.0	1.50	"	"	3.0	1.56
8	3.4	1.70	"	"	3.2	1.64
9	3.6	1.80	"	"	3.3	1.70
10	4.0	2.00	"	"	3.5	1.82
11	4.5	2.25	"	"	4.1	1.96
12	5.0	2.50	"	"	4.8	2.11
13	6.0	3.00	"	"	7.0	2.40
14	6.5	3.25	"	"	8.3	2.54
15	7.0	3.50	"	"	9.4	2.68
16	8.0	4.00	"	"	11.0	2.96
17	9.0	4.50	"	"	14.0	4.89
18	10.0	5.00	"	"	17.0	5.34

Table 2 Typical Physical Properties

Run No.	BEQ	Viscosity, cS		Viscosity Index	Specific Gravity (15/4°C)
		210° F	100° F		
1	1.5	883.5	—	—	1.0774
2	2.0	263.1	—	—	1.0760
3	2.2	179.0	10,456	92	1.0736
4	2.4	134.1	6,491	90	1.0712
5	2.6	141.3	6,963	91	1.0732
6	2.8	114.6	5,143	88	1.0700
7	3.0	115.0	5,384	86	1.0766
8	3.4	206.1	—	—	1.1073
9	3.6	130.4	7,409	81	1.0914
10	4.0	157.0	8,978	88	1.0999
11	4.5	170.8	10,594	88	1.1040
12	5.0	344.8	—	—	1.1194
13	6.0	179.7	10,006	94	1.1037
14	6.5	381.8	—	—	1.1049
15	7.0	307.7	—	—	1.0938
16	8.0	251.0	—	—	1.1198
17	9.0	259.7	8,561	114	1.0625
18	10.0	162.7	4,047	114	1.0605

Table 3 Typical Analysis

Run No.	BEQ	Alkalinity Value (KOH mg/g)	Ca (wt%)	CO ₂ (wt%)	S (wt%)	Free-POP (wt%)	Free-LA (wt%)
1	1.5	213	7.66	4.01	7.28	0.2	—
2	2.0	223	8.29	5.28	6.14	0.2	0.1
3	2.2	226	8.11	5.72	5.93	0.2	—
4	2.4	232	8.30	5.87	5.53	0.1	0.2
5	2.6	234	8.34	6.03	5.58	—	—
6	2.8	234	8.40	6.07	5.37	0.1	—
7	3.0	246	8.75	6.70	5.15	—	—
8	3.4	278	9.87	7.79	5.15	—	—
9	3.6	266	9.56	7.76	4.78	0.2	—
10	4.0	279	10.0	8.05	4.61	0.2	—
11	4.5	293	10.9	8.47	4.30	—	—
12	5.0	317	11.6	8.52	4.00	—	—
13	6.0	311	11.1	8.71	3.48	0.3	0.1
14	6.5	317	11.2	8.51	3.23	0.3	1.7
15	7.0	311	11.0	8.17	2.93	—	2.1
16	8.0	343	12.2	9.99	2.65	—	0.9
17	9.0	288	10.3	8.18	1.71	—	0.8
18	10.0	283	10.1	8.25	1.74	—	1.7

a dark yellowish red transparent liquid product (V) was obtained. Characteristics of thus obtained product and of other samples are shown in **Tables 2** and **3**.

2.3 Analysis and Calculation

The Ca content, CO₂ content as carbonate and S content of the products were determined by the EDTA chelating and modified IP 111/49T methods, Rimmer's method⁸⁾, and ASTM D 1552—64, respectively. The composition of the distillates was analyzed by both gas chromatography and Karl-Fischer's method (ASTM D 1744—60T). The free POP and LA contents in the products were also analyzed by gas chromatography. The contents of both ligand components, EG and POP, in the products were obtained from the material balance.

2.4 Isolation of 2.0 BEQ Active Ingredient

The CO₂-treated mixture (III) with an alkalinity value of 118 (KOH mg/g) was used as a starting material for this purpose.

551.5 g of the mixture (III) was filtered through a filter paper (Toyo Roshi No. 5A grade) after removal of a major portion of insolubles by centrifuge (3,000 rpm × 30 min) at room temperature to give 546.5 g of a clear filtrate (VI).

To 236.4 g of the filtrate diluted with an approximately equal volume of methylethyl ketone (JIS guaranteed reagent), a large amount of ethyl alcohol (JIS guaranteed reagent) was added dropwise while stirring, until alkalinity value of the liquid phase decreased to 2, to give a suspension. A precipitate was isolated from the above suspension by centrifuge (3,000 rpm × 30 min) and dried *in vacuo* (1 mmHg) at 80 °C for 2 hours to give 68.7 g of a crude amorphous

substance (V).

68.1 g of the substance (V) was dissolved in 150 ml of toluene (JIS guaranteed reagent), reprecipitated by addition of ethyl alcohol, collected by centrifuge, washed with ethyl alcohol, and recollected by centrifuge. This series of refining processes was repeated three times. Then, after drying at 80°C under 1 mmHg for 25 hours, the substance obtained was dissolved in a small amount of benzene (JIS guaranteed reagent), followed by freeze-drying under 1 mmHg, and finally by vacuum drying (1 mmHg) at 110°C for 50 hours to give 50.9 g of a yellow amorphous powdered material, which is the active ingredient (VII).

The yield of (VII) based on (V) was 74.7%. Anal. for (VII); C, 41.2; H, 5.8; S, 8.1; Ca, 17.1.

2.5 Ebulliometric Observation

For this investigation, the 2.0 BEQ active ingredient (VII) was measured with a Takara twin type ebulliometer Model L-4 having a sensitivity of $\pm 5 \times 10^{-5}^{\circ}\text{C}$. **Table 4** shows the apparatus constants experimentally determined

Table 4 Apparatus Constants

Standard Sample	Molecular Weight	Apparatus Constants (deg/mol/1,000g)	
		Benzene	1, 2-Dichloroethane
Naphthalene	128.2	2.53	3.16
Polyethylene	4.8×10^3	—	3.15
Reference (Ebullioscopic constant)	—	2.54 ^{a)}	3.27 ^{b)}

a) Reference 4a).

b) Reference 4b).

in two solvents, benzene (JIS guaranteed reagent) and 1,2-dichloroethane (JIS guaranteed reagent), by use of naphthalene (JIS guaranteed reagent) and polyethylene (Standard sample of Takara Thermistor Instruments Co., Ltd.).

3 Results

3.1 Ebullioscopic Results

The ebullioscopic results on a benzene solution and 1,2-dichloroethane solution of 2.0 BEQ active ingredient (VII) are shown in **Figs. 1** and **2**. ΔT_b is the boiling-point elevation and C is the concentration (mg/g) of the solute in the solution. **Fig. 1** shows a plot of $\Delta T_b/C$ vs. C in the benzene solution. The plotted line is curved at concentration less than 1.4 mg/g and it becomes linear with concentrations greater than 1.5 mg/g. Therefore, on the basis of the reduced boiling-point elevation given by extrapolating the straight line to zero concentration, the apparent number-average molecular weight of the solute was calculated to be 25,400.

Fig. 2 shows a plot of $\Delta T_b/C$ vs. C in the 1,2-dichloroethane solution. The plotted line is straight at concentrations less than 5 mg/g, but it is curved at concentrations greater than 7 mg/g. In the region of the curve, many particles of undissolved ingredient were observed visibly in the solution. The apparent number-average molecular weight of the solute calculated from the straight portion of the line in **Fig. 2** was about 2,900.

3.2 Composition of Products

Fig. 1 Ebullioscopic Behavior of 2.0 BEQ Active Ingredient in Benzene

Fig. 2 Ebullioscopic Behavior of 2.0 BEQ Active Ingredient in 1,2-Dichloroethane

The results of both chemical analysis and material balance are summarized in **Tables 3** and **5**, respectively. **Fig. 3** shows a plot of molar ratio of ligand component EG to ligand component POP vs. PEQ of the product. **Fig. 4** shows a plot of molar ratio of ligand component CO_2 to ligand component POP vs. PEQ of the product. PEQ represents the number of equivalents of calcium per equivalent of ligand component POP in the product. In **Fig. 5**, alkalinity values of the active ingredients calculated from the data in **Tables 3** and **5** are plotted against their PEQ.

3.3 Conversion of Raw Materials into Products

In **Table 6**, the conversion of CaO, S and POP

Table 5 Ligand Components POP and EG, and OIL-Component in Products (Calcd.)

Run No.	BEQ	Ligand Component		OIL-Component (wt%)
		POP (wt%)	EG (wt%)	
1	1.5	43.6	3.9	32.2
2	2.0	35.2	5.8	38.3
3	2.2	31.6	6.3	41.9
4	2.4	30.4	6.2	41.5
5	2.6	28.6	6.4	43.8
6	2.8	27.0	6.8	45.1
7	3.0	25.2	9.3	44.7
8	3.4	24.1	5.8	46.0
9	3.6	22.2	7.4	47.1
10	4.0	22.5	7.1	46.5
11	4.5	21.5	8.5	45.4
12	5.0	19.7	6.9	47.4
13	6.0	20.0	8.9	45.0
14	6.5	19.1	9.1	44.8
15	7.0	18.1	8.9	45.6
16	8.0	16.1	10.3	43.7
17	9.0	12.0	7.4	56.0
18	10.0	11.2	7.2	56.9

PEQ; the number of equivalents of Ca per equivalent of POP in products

Fig. 3 Molar Ratio of Ligand Component EG to Ligand Component POP in Products

Fig. 4 Molar Ratio of Ligand Component CO_2 to Ligand Component POP in Products

Fig. 5 Alkalinity Value of Active Ingredient

into each product is summarized. The conversion of both CaO and S is nearly constant in this series, and it is on the average 94.7% and 77.5%, respectively. The conversion of POP, however, decreases gradually from 80.9% to 74.7% with increase of BEQ from 1.5 to 3.6 and then increases gradually up to 99.9% with increase of BEQ from 3.6 to 10.0.

3.4 BEQ and PEQ

In Fig. 6, BEQ which means the number of equivalents of CaO blended per equivalent of POP blended is plotted against PEQ, which means the number of equivalents of calcium per equivalent of ligand component POP in the product. The plots appear to fit on a straight line with a slope of 1.0, but in the region of greater than 6.0 BEQ, the values of PEQ are slightly lo-

Table 6 Conversion of Starting Materials into Products

Run No.	BEQ	Ca (%)	POP (%)	S (%)
1	1.5	98.8	80.9	66.8
2	2.0	96.3	82.2	70.7
3	2.2	97.6	80.6	74.4
4	2.4	97.4	84.2	75.7
5	2.6	94.8	81.2	78.4
6	2.8	92.7	79.7	78.2
7	3.0	93.8	77.3	78.0
8	3.4	95.6	75.1	79.5
9	3.6	92.8	74.7	79.5
10	4.0	91.8	78.2	79.4
11	4.5	93.7	82.3	81.4
12	5.0	95.2	79.4	79.6
13	6.0	92.1	95.7	82.4
14	6.5	94.4	99.3	83.3
15	7.0	90.4	99.4	79.8
16	8.0	96.2	98.1	79.6
17	9.0	97.1	99.1	70.7
18	10.0	93.8	100.0	76.9

BEQ; the number of equivalents of CaO blended per equivalent of POP blended

Fig. 6 PEQ vs. BEQ of Products

(); PEQ of product

Fig. 7 Viscosities of Products

wer than those of BEQ, whereas in the region of less than 6.0 BEQ those of PEQ are slightly higher than those of BEQ.

3.5 Physical Properties of Products

Table 2 shows typical physical properties of

the products, over-based sulfurized calcium phenates of from 1.5 to 10.0 BEQ.

They have a viscosity index of about 88 in common except the 6.0 to 10.0 BEQ products having an index of 94 to 114, and their specific gravity is about 1.1.

Fig. 7 shows a plot of the viscosities *vs.* alkalinity values of the products.

4 Discussion

The active ingredients of the over-based phenates in this series are rather unstable in an isolated state or with increasing BEQ. Therefore, the relatively stable 2.0 BEQ active ingredient was isolated (yield; about 70%) and used for study on ebullioscopic behavior.

From **Fig. 1**, it is seen that in the case of the benzene solution of the active ingredient, a plot of $\Delta T_b/C$ *vs.* C curves gradually upward along the $\Delta T_b/C$ axis with decreasing concentration of the solute. This result will suffice to show that the apparent molecular weight of the solute varies with concentration, in other words, the active ingredient exists in a micellar form⁶⁾ in the benzene solution. Whereas **Fig. 2** shows that the plot in the 1,2-dichloroethane solution is linear in the region of low concentrations of 0.05 to 0.5 mg/g, but at about 0.7 mg/g the plot curves downward along the $\Delta T_b/C$ axis. This is undoubtedly due to the presence of undissolved active ingredient. Moreover, since the solubility parameter of 1,2-dichloroethane ($\delta=9.86$) is greater than that of benzene ($\delta=9.16$)⁵⁾, it does not seem plausible that, in the 1,2-dichloroethane solution, CMC is present in the region of concentration of 0.04 mg/g or less⁷⁾. Clearly, the active ingredient exists in a monomolecular form in the region of the straight portion of the line in the 1,2-dichloroethane solution. Therefore, it can be said that the active ingredient has a number-average molecular weight of 2,900 and forms a micelle of an aggregation number of about 8.8 in the conditions described in the benzene solution.

If the active ingredient has a structure similar to the one suggested by Smalheer et al.^{2),3)}, the structure should be expressed as $(C_8H_{17}C_6H_5O)_2S_{2.2}Ca \cdot CaCO_3$, and the apparent number-average molecular weight should be 450~650. Hence, it may be concluded that the actual structure of the active ingredient in this series is quite different from the structure proposed by Smalheer et al.

From the material balance, as in **Tables 3** and **5**, it has been revealed that the active ingredients, without exception, consist of calcium and four ligand components of S, POP, CO_2 and EG. Since S and POP presumably exist mostly in a sulfurized POP form⁹⁾, bi- or oligo-functional-ligand components are seemingly predominant in the active ingredients of this series. This may be pointed out as one of the reasons for the polymer formation.

Figs. 3 and **4** show that, with an increase in PEQ which means the number of equivalents of calcium per equivalent of POP in the products and is symbolized as P_p , the proportion of two ligand components EG and CO_2 in the active ingredient increases compared with that of ligand component POP. This apparently implies that the above two ligand components play an important role with the calcium atom in the formation of so-called "skelton of over-based part". In addition, the continuous linear relationships as seen in **Fig. 3** and **4** indicate that the active ingredient of this series is a mixed homolog, a mixture consisting of compounds of composition differing successively by a constant amount of a certain constituent such as EG, CO_2 and Ca.

Moreover, from these results the derivation of quantitative relationships between the changes of composition and PEQ, which is useful for classification of these over-based phenates, is allowed. Thus, if $[EG]$, $[CO_2]$ and $[POP]$ are the numbers of moles of the respective ligand components, the linear relationships in **Figs. 3** and **4** are analytically expressed by the least-squares method as follows.

$$[EG]/[POP] = 0.24P_p + 0.01 \quad (1)$$

$$[CO_2]/[POP] = 0.39P_p - 0.19 \quad (2)$$

Then, if the number of moles of calcium in the products is $[Ca]$, PEQ can be written as $P_p = 2[Ca]/[POP]$ (3)

Therefore, the quantitative relation among the three ligand components, calcium atom and PEQ in a given product in this series is given by eq. (4) from eqs. (1), (2) and (3).

$$\{[EG] + [CO_2] + [POP]\}/[Ca] = 1.64/P_p + 1.26 \quad (4)$$

This eq. (4) shows that the molar ratio of all the ligand components (EG, CO_2 , POP) to calcium varies in a hyperbolic manner with increasing PEQ, as in **Fig. 8**. Considering the fact that the skelton consisting of small ligand com-

Fig. 8 Molar Ratio of Ligand Components to Calcium in Products

ponents increases with increase of PEQ (or BEQ), this result may well illustrate the fact that alkalinity value of the active ingredient in this homologous series increases with increase of PEQ to approach to a constant value as in **Fig. 5**.

Moreover, a similar trend is observed in the case of the alkalinity value of the product, where its viscosity remains constant. But the trend in this case disappears in 6.5 or more BEQ products. This seems to be the reason for the change of the micellar structure, and suggests that a viscosity character of "polymer" in the molecule of the active ingredient is quite masked by the micelle in 6.0 or less BEQ products. The change of the viscosity index of the product also supports the above interpretation.

5 Conclusions

The foregoing results relating the over-based sulfurized calcium phenates containing calcium of from about 150 to 1,000% on the basis of the theoretical amount prepared by using CaO, POP, S, EG, CO₂, LA and OIL as starting materials lead to the following conclusions.

1) From ebullioscopic results, the active ingredient of the phenate is amphipathic polymer.

2) From the material balance, the following conclusions are obtained. The active ingredient consists of Ca and four ligand components, *i.e.*

POP, S, EG and CO₂. The molar ratio of small ligand component EG or CO₂ to large one POP varies linearly as the number of equivalents of calcium per equivalent of POP, *i.e.* PEQ. This result indicates the active ingredient to be a mixed homolog. Moreover, the molar ratio of ligand components, the sum of POP, EG, and CO₂, to Ca varies inversely as PEQ in a hyperbolic manner. These results account for the trend that alkalinity values of the active ingredients increase with the increase of PEQ to approach to a constant value.

3) From the changes of both the alkalinity values of the phenates, where their viscosities remain constant, and their values of viscosity index, it is suggested that their micellar structures change before and after 6.0~6.5 BEQ (or PEQ).

In closing, it may be said that, presumably, the phenates are the oil-solutions of mixed homologs of an amphipathic coordination-condensation polymer homologous series.

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