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METAL-CONTAINING POLYETHYLENE WAXES

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ABSTRACT

Low molecular weight polyethylene resulting as a by-product in a high density polyethylene plant was subjected to controlled oxidation and subsequent modification to convert the free carboxyl groups into calcium carboxylate groups. Several wax grades with useful properties and applications have thus been obtained.

INTRODUCTION

Polyethylene (PE) waxes, i.e., low molecular weight polyethylenes, are useful materials in various applications. PE waxes available on the market are usually polymers of 1000 to 6000 molecular weight obtained by telomerization, i.e., the polymerization of ethylene under conditions able to assure only the formation of low molecular polymers. No information seems to be available about the use of PE waxes originating as by-products in the PE plants. It was the purpose of this work to develop metal-containing PE waxes based on such by-products. Metal- or ion-containing polymers are often complicated structures developed for sophisticated tailor-made applications [1–3]. However, even very simple structures, such as those of the metal-containing PE waxes, may have interesting and useful properties.

EXPERIMENTAL

A by-product of a high-density PE plant (slurry process) was used as the raw material without further purification. The PE wax was first oxidized in order to obtain free carboxyl groups attached to the polymer backbone. Metal-containing PE waxes were then obtained by the reaction between the oxidized PE wax (OXPE) and metallic hydroxides. Due to the low molecular weight of the PE wax $\overline{M}_n = 1000$, vapor pressure osmometry, 80°C, toluene; and ($\overline{M}_v = 3000$, viscometry, 130°C, decaline) and its low melt viscosity (10–30 cP at 130°C), both oxidation and saponification were performed in vessels fitted with a usual impeller-type stirrer. The oxidation of the PE wax was carried out by bubbling air into the polymer melt maintained under stirring at temperatures from 130 to 170°C. Then the hydroxide was added to the stirred melt of the OXPE wax. In order to favor the elimination of water resulting from the neutralization reaction, nitrogen was bubbled continuously into the polymer melt.

RESULTS AND DISCUSSION

Synthesis of Oxidized Polyethylene Waxes

The oxidation of the PE wax occurred via a free-radical reaction mechanism, in the same manner as the oxidation of paraffins for the preparation of fatty acids [4]. The first reaction steps involved the formation of PE macroradicals ($PH \rightarrow P\cdot$), peroxy macroradicals ($P\cdot + O_2 \rightarrow POO\cdot$), and macrohydroperoxides ($POO\cdot + PH \rightarrow POOH + P\cdot$). Then, by the thermal decomposition of this hydroperoxide and during different subsequent reactions, various oxygen-containing compounds appeared in the reaction mixture: ketones, alcohols, aldehydes, α-ketone-peroxides, acids, peracids, esters, diketones, and anhydrides. However, the final oxidation product contained practically only free carboxyls and ester groups. The content of these groups in the OXPE wax was measured by acidity and saponification indices (AI and SI), respectively.

The infrared (IR) and nuclear magnetic resonance (^{1}H-NMR) spectra of the OXPE waxes showed the presence of the carbonyl groups: the strong absorption band at 1720 cm^{-1} and the resonance line at 2.2 ppm, respectively (Fig. 1). The intensity of both absorption bands and resonance lines followed the degree of oxidation. Thus, the following linear relationship was found: $E_{1720}/E_{1460} = 0.00558$ SI, where E_{1720} is the extinction of the analytical band ($\nu C{=}O$), E_{1460} is the extinction of a refer-

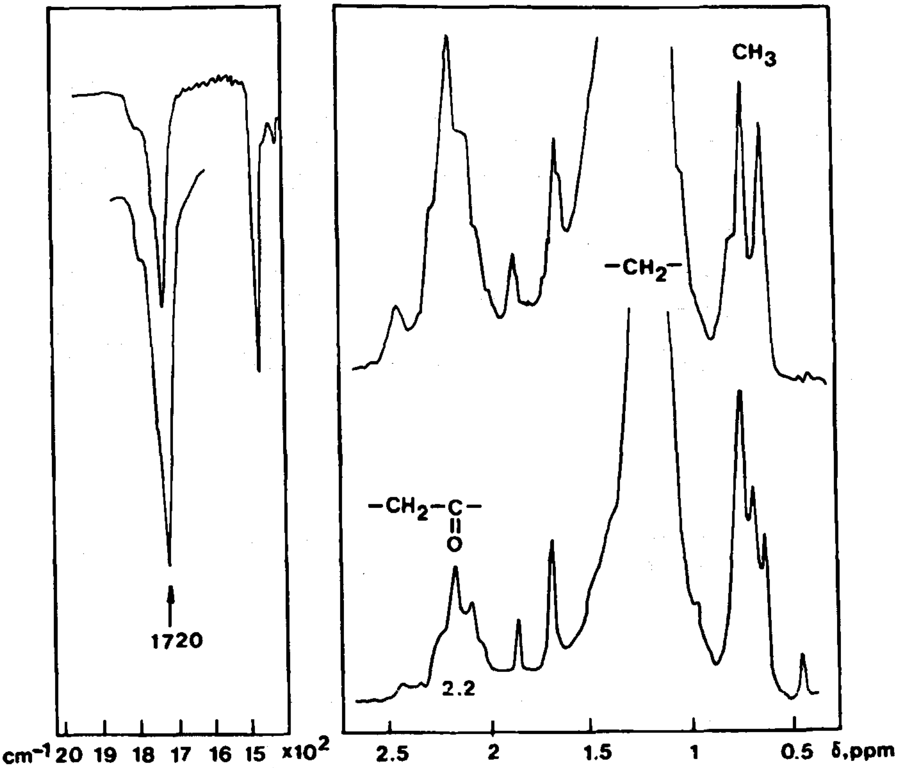

FIG. 1. The IR- and ^{1}H-NMR spectra of two samples of OXPE wax with different oxidation degrees: (left) AI = 30 mg KOH/g, (right) AI = 55 mg KOH/g.

ence band (δCH_2), and SI is the value of the saponification index (mg KOH/g).

When antioxidants with a hindered phenolic structure or amine-type antioxidants were added to the PE wax, an increased induction period and a lower oxidation rate were noticed. On the other hand, in the presence of free-radical generators, especially organic peroxides such as dibenzoylperoxide and dicumylperoxide, the oxidation proceeded faster. These results emphasized the free-radical mechanism of the PE wax oxidation.

From the technical point of view, the oxidation of the PE wax was followed by measuring the acidity and saponification indices from time to time. Following a short induction period, a linear relationship between both acidity and saponification indices and the oxidation time was found (Fig. 2). The slope of each curve depended on the reaction conditions, i.e., temperature, air flow rate, and catalysts. For the same reaction conditions, the rate of the oxidation process depended on the size of the oxidation vessel. Higher oxidation rates and better reproducibility were obtained in a pilot scale plant (1 m^3 capacity) than in laboratory scale vessels (1-15 L).

During the oxidation of the PE wax, degradation of the polymer chains also occurred to some extent. However, only a slight decrease of the molecular weight due to splitting of polymer chains was noticed. No crosslinking of the polymer chains occurred during oxidation. The drop point of the PE wax slightly decreased with the oxidation time until it reached a constant value (Fig. 2).

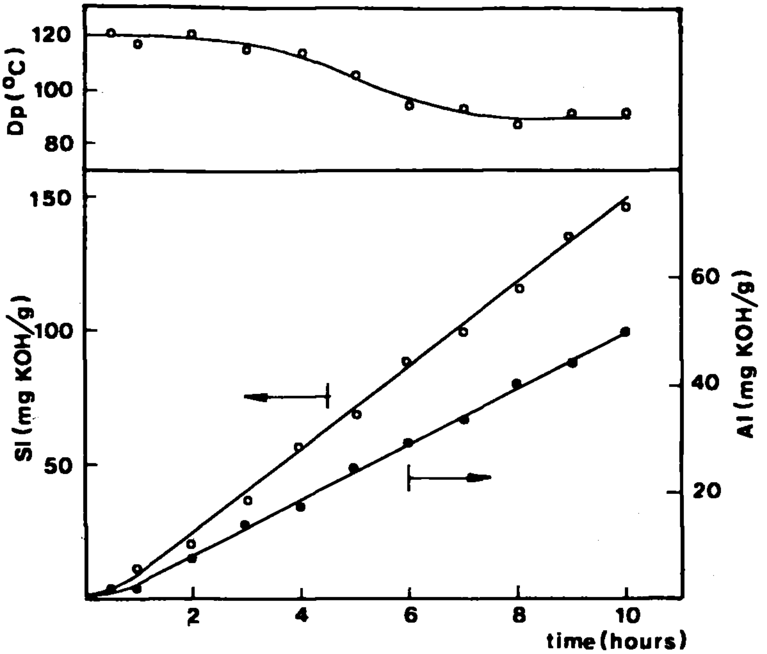

FIG. 2. The dependence of acidity index (AI), saponification index (SI), and drop point (Dp) of the PE wax on the oxidation time.

Synthesis of Metal-Containing Polyethylene Waxes

Metal soaps, i.e., salts of fatty acids such as stearates, palmitates, and myristates (Me: Al, Ba, Ca, Cd, Mg, Zn) are obtained by a two-step process. First the fatty acid is converted into its Na salt by a reaction performed in hot water or a water/alcohol mixture. Then, by adding into the resulting solution a salt of the desired metal (sulfates, chlorides, acetates, nitrates) the metal soap was precipitated. However, this approach is not suitable to obtain metal-containing PE waxes. Therefore, an attempt was made to develop a more convenient synthesis method, i.e., the direct reaction of the OXPE wax with metallic compounds [5]. The obtaining of calcium-containing PE waxes was thus studied. The reaction was performed by adding a Ca compound into the OXPE wax and maintaining the melt under stirring. The free carboxyl groups of the OXPE wax were neutralized by the Ca compound, and the reaction was followed by measuring the decreasing acidity index.

No reaction occurred with calcium carbonate or calcium oxide. On the contrary, when calcium hydroxide was added into the melt, a decrease of the initial acidity index of the OXPE wax was noticed (Table 1). The IR spectrum clearly showed the formation of the carboxylate bonds, i.e., two absorption bands at 1565 and 1410 cm^{-1} due to the symmetrical and asymmetrical stretching vibrations of the COO^- groups, respectively (Fig. 3). The temperature of the wax melt seemed to have no influence on the reaction yield. The neutralization reaction was very fast, so that increasing the reaction time over 30 min was unnecessary (Table 1).

Starting from OXPE waxes of different acidity indices and adding increasing proportions of $\mathrm{Ca(OH)_2}$, a linear relationship between the values of the acidity index and the content of $\mathrm{Ca(OH)_2}$ was found (Fig. 4). The resulting straight lines have the same slope, i.e., a decrease of the acidity index of about 11.3 mg KOH/g per one part $\mathrm{Ca(OH)_2}$ added to 100 parts OXPE wax. This value corresponded to the theoretical one, i.e., the value resulting from the stoichiometric reaction between two carboxyl groups and a $\mathrm{Ca(OH)_2}$ molecule. The formation of the Ca carboxylate groups occurred only by the neutralization of COOH groups and not by the saponification of the ester groups.

The formation of carboxylate groups was also followed by IR spectroscopy by using the ratio between the extinction of the analytic band at 1565 cm^{-1} due to the symmetrical stretching vibration of the COO^- group and the extinction of a reference band at 1460 cm^{-1} due to the $\mathrm{CH_2}$ groups of the PE chain (Fig. 3). This ratio increased linearly with the proportion

TABLE 1. Synthesis of Calcium-Containing PE Waxes

Oxidized PE wax		Calcium compound					
AI, mg KOH/g	SI, mg KOH/g	Type	p/100 p OXPE	Temperature, °C	Time, h	Saponified AI, mg KOH/g	PE wax SI, mg KOH/g
33.9	115	$CaCO_3$	1.0	135	1.0	30.7	102.4
33.9	115	CaO	1.0	135	1.0	27.6	110.9
33.9	115	$Ca(OH)_2$	1.0	135	1.0	9.5	108.3
48.4	113	$Ca(OH)_2$	3.5	130	1.0	11.9	98.8
48.4	113	$Ca(OH)_2$	3.5	152	1.0	14.8	96.5
48.4	113	$Ca(OH)_2$	3.5	175	1.0	15.5	98.1
38.9	108	$Ca(OH)_2$	1.0	135	0.5	14.2	84.3
38.9	108	$Ca(OH)_2$	1.0	135	1.0	14.3	83.5
38.9	108	$Ca(OH)_2$	1.0	135	2.0	14.1	86.1
38.9	108	$Ca(OH)_2$	1.0	135	3.0	13.9	85.0
38.9	108	$Ca(OH)_2$	1.0	135	4.0	14.0	84.8
38.9	108	$Ca(OH)_2$	1.0	135	5.0	13.5	86.3

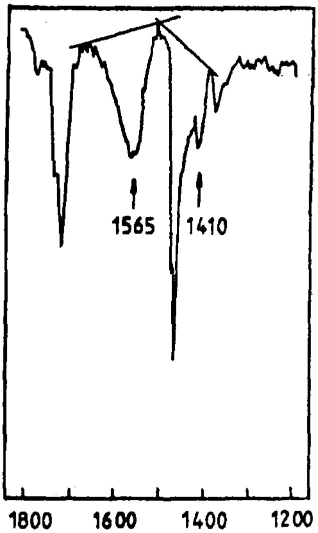

FIG. 3. The IR spectrum of a Ca-containing PE wax (AI = 0 and SI = 60 mg KOH/g, 2.2% Ca).

of the added hydroxide, i.e., mg $Ca(OH)_2$/g wax = $37.4E_{1565}/E_{1460}$, following the linear decreasing of the acidity index due to the disappearance of the carboxyl groups and the appearance of the carboxylate bonds (Fig. 4).

Potential Applications of Calcium-Containing PE Waxes

A wide range of Ca-containing PE waxes with different acidity index values and calcium contents have been obtained by the proper choice of the OXPE wax type, i.e., the degree of oxidation and the proportion of added $Ca(OH)_2$. Useful properties and, consequently, applications were found for some of them. OXPE waxes partly saponified with $Ca(OH)_2$ were tested as lubricants for plastics, release agents, solvent-based polishes, and especially pastes. Thus, a Ca-containing PE wax (AI = 13.9 mg KOH/g, SI = 78 mg KOH/g, 1.4% Ca) was tested as a lubricant for poly(vinyl chloride) in comparison with a partially saponified montan wax of similar characteristics (AI = 12.5 mg KOH/g, SI = 100 mg KOH/g, 1.6% Ca). A mixture obtained by dry blending 100 parts rigid suspension-grade PVC (*K* value 58), 2 parts of thermal stabilizer (dibasic lead stearate), and 0.2–1.5 parts of wax lubricant was charged into a torque-rheometer mixing head (Brabender Plasticorder). The rheometer

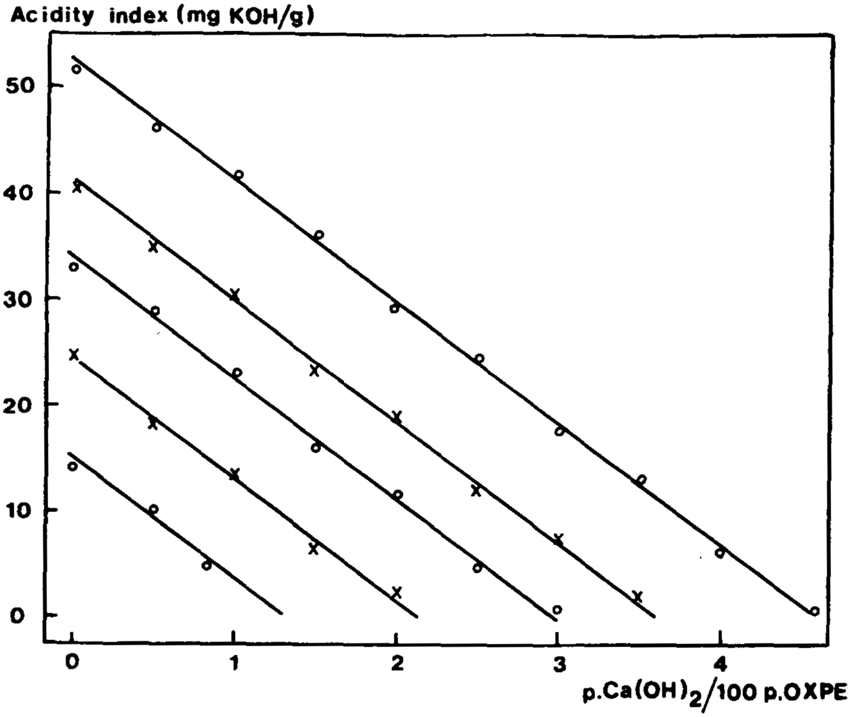

FIG. 4. Acidity index versus $Ca(OH)_2$ proportion added into the OXPE wax.

chart of torque vs time first showed an increase to a maximum torque and then a decrease to a minimal torque due to the beginning of fusion. As the PVC particles fused and formed a plastic melt, the torque increased again to a peak, called the fusion peak; the time required to reach this peak is called the fusion time.

Depending on structure and composition, lubricants reduce the adhesion of polymer melts to hot metal surfaces and friction at hot machine parts (external lubricating effect) or they improve the flowability of polymer melts (internal lubricating effect). The lower values of minimum torque and the longer fusion times for the saponified OXPE wax showed that it is a more "external" lubricant than the saponified montan wax (Table 2). Indeed, montan waxes are based on montanic acids which predominantly consist of straight chain and saturated carboxylic acids

TABLE 2. Brabender evaluation of Waxes as PVC Lubricants

Wax type	Wax concentration, p/100 p PVC	Maximum torque, Nm	Minimum torque, Nm	Fusion time, min	Melt temperature, °C
PE	0.2	30.6	25.2	0.66	128
MO	0.2	31.4	25.0	0.70	128
PE	0.4	24.7	12.7	1.57	134
MO	0.4	27.6	18.3	1.00	133
PE	0.6	25.2	9.6	2.40	132
MO	0.6	28.5	20.6	1.10	130
PE	0.8	20.4	7.5	4.73	132
MO	0.8	22.1	11.3	2.16	132
PE	1.0	18.6	6.9	5.60	136
MO	1.0	22.9	13.4	2.13	134
PE	1.5	15.7	4.9	9.20	138
MO	1.5	19.1	9.3	3.20	130

with chain lengths of C_{28}–C_{32}. The longer nonpolar chains in the Ca-containing PE sample are responsible for the more external lubricating effect.

Calcium-containing PE waxes have also been found useful as acid scavengers in polyolefins and as corrosion inhibitors, matting agents, and antisettling agents in various laquer and paint systems in organic solvents.

CONCLUSIONS

Controlled oxidation of low molecular weight PE and subsequent modification by converting the carboxyl groups of the OXPE waxes into calcium carboxylate groups allowed us to obtain several wax grades with useful properties and applications from this by-product of a HDPE plant. The synthesis, characterization, and testing of other metal-containing PE waxes (Me: Mg, Ba, Zn, Al) is under progress and will be reported later.

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