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PREPARATION AND CHARACTERIZATION OF PVC STABILIZERS: BASED ON MIXTURE OF ZINC, CALCIUM AND BARIUM SALTS OF THE CARBOXYLIC ACID

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Different types of PVC stabilizers based on different divalent metals salts of the long chain fatty acids from various oils. Sunflowers oil based composition having Zn/Ca in the ratio of 1:1 and 1:1.5 showed good results. The other oils coconut oil, soyabean oil and linseed oil did not show encouraging results. The ratio between zinc and barium should not exceed 1:2 in case of soyabean oil. All the results were compared with imported stabilizer (ICI).

INTRODUCTION

Different types of stabilizers have already been used in PVC composition. These are usually stearates of metals like Ba, Cd, Zn, Ca, Pb, etc. [1] Sometimes as a single compound, sometime in compound formulation [2]. Recently mixed stabilizers which are synergistic mixture of metal compound of group-II (Ca, Cd, Ba, Zn) are in use. These mixtures are very much effective. [3] Comparative studies have been carried out between different types of stabilizers, but the best results have been obtained when barium-zinc based stabilizers have been used. [4].

It has been observed that Pd and organotin stabilizers were most effective during thermal aging where as cadmium stearates, calcium stearates mixtures were more effective during photo degradation [7].

It has been observed that in Pb stabilized systems the unsaturation in the polymers increases as a result of degradation, but in Ba, Cd, Zn stabilized systems the unsaturation appeared very slowly. [8]. It has been observed that magnesium stearates and alkali metal carbonate exhibits synergism as heat stabilizer for resins such as PVC. [9]

The synergistic effects was most pronounced for the initial colour of PVC compound where Ca and Zn complexes were used for stabilization. Optimum results were obtained when 25% primary stabilizer (Ca/Zn complex) was replaced by about 10% of each co-stabilizer. [10]

The melt flow index increased and the physicochemical properties and resistance to photo thermal aging of plasticized PVC compound for leather coating were improved by stabilization with a 0.15:0.85 eutectic mixture of Ca-stearate and Cd-stearate [11].

The co-precipitation of metallic salts gave very encouraging results. The metal soaps and lead salts were co-precipitated in water to a slurry which was spray dried. PVC compounded with this material remained stable for 83 min at 180°C [16]

Ba and Cd soaps of synthetic C_5-C_9 fatty acids were effective stabilizers for PVC. Ba and Cd epoxy stearates, benzoates, salicylates and stearates were less effective [17].

Polyvinyl chloride stabilizers having good quality was prepared by heating mixtures of CdO, ZnO, PbO, $Ba(OH)_2$, and $Ca(OH)_2$ with C_5-C_{20} carboxylic acid fraction at 60-130°C in the presence of Ca-alkyl benzene sulfonate [19]. The formation of chloride and polymer coloration during thermal degradation of PVC stabilized with a zinc/calcium recipe has been studied. [20]

EXPERIMENTAL AND PROCEDURE

Coconut oil, soyabean oil and sunflower oil were used as purchased. Linseed oil was extracted from the seeds.

Zinc chloride, barium chloride, calcium chloride (BDH) sodium hydroxide, hydrochloric acid toluene (commercial) were used without further purification. Reference stabilizer (ICI metal complex stabilizer) was used.

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PROCEDURE

Preparation of fatty acid mixture from the oils. Sodium hydroxide (30 g) in 50 cm^3 distilled water was added slowly to 140 g of oil at 180-200°C. The saponification resulted was completed by vigorous stirring at 200°C for 25 minutes. After cooling to 30°C, the mixture was shaken with excess distilled water. Two layers were obtained and the upper layer containing the fatty acid salts was removed and neutralized with 1:1 HCl to form the free acids which were removed with a separating funnel. The yields of mixed fatty acids based on the original weight of oil were – coconut oil 69%, linseed oil 79%, soyabean oil 79% and sunflower oil 86%.

Characterization of stabilizer. The stabilizer was characterized by making a compound of polyvinylchloride, and stabilizer with following composition:

Polyvinylchloride powder = 3 grams
Stabilizer ..... = 0.09" (3%)

Then heated for fifteen minutes at different temperatures (150-180°C) to study the thermal property of stabilizer in oven. The results are shown in Tables (1, 2, 3, 4).

Preparation of salts of divalent metals with free fatty acids. 'Mixtures of zinc and barium and of zinc and calcium salts of fatty acids were prepared by adding 3 g of mixed chlorides in 10 cm^3 water to 10 g of the fatty acids at 200-220°C. After 15 min with continuous stirring, the mixture was cooled to 30°C, shaken with excess distilled water, and the upper layer of mixed fatty acid salts separated. The mixed salts were found to be soluble in tetrahydrofuran, chloroform, carbon tetrachloride, xylene and tolune. For use as stabilizers, a clear solution of 4 g in 10 cm^3 toluene was used'.

Results

Table-1. Stabilizers based on coconut oil in the absence of plasticizer
The samples were kept 15 minutes on each temperature

No.	Compositions Zn	Bs	Colours at 150°C	160°C	170°C	180°C
1	3	2:1	Blakish	Bluish black	Dark bluish black	Black
2	5	1.5:1	No change	Light green	Brownish grey	Black
3	1	1:1	Light grey	Dark grey	Sandy black	Black
4	4	1:1.5	White	Off white	Off white	Black
5	2	1:2	Blakish	Black	Dark black	Black
	Zn	Ca				
6	8	2:1	Light grey	Grey	Sandy grey	Black
7	10	1.5:1	Creamy	Creamy	Whitish cream	Black
8	6	1:1	Light biscuit	Cream	Cream	Black
9	9	1:1.5	White	Off white	Greyish white	Black
10	7	1:2	Slight yellow	Light yellow	Yellow	Black
11	11	Reference	Creamy	Cream	Pinkish cream	Black

Preference: Zn Ca 1:1, Zn Ca 1:2, Zn Ca 1.5:1 compositions are acceptable.

Therefore the amount of calcium should not more than double to zinc amount.
The zinc/calcium ratio should not exceed 3:4.

Table-2. Stabilizers based on soyabean oil in the absence of plasticizer
The samples were kept 15 minutes on each temperature

No.	Compositions Zn	Ba	Colours at 150°C	160°C	170°C	180°C
1	3	2:1	Fine white	White	Off white	Black
2	5	1.5:1	White	Dirty white	Dirty white	Black
3	1	1:1	Pale yellow	Yellow	Yellow	Black
4	4	1:1.5	Fine white	White	White	Black
5	2	1:2	Light pale yellow	Pale yellow	Pale yellow	Black
	Zn	Ca				
6	8	2:1	White	Dirty white	Dirty white	Black
7	10	1.5:1	Off white	Off white	Off white	Black
8	6	1:1	Off white	Light pale yellow	Pale yellow	Black
9	9	1:1.5	Off white	Pale yellow	Pale yellow	Black
10	7	1:2	Off white	Off white	Dirty white	Black
11	11	Reference	Creamy	Creamy	Pinkish cream	Black

Preference: Zn Ba (1:1) Zn Ba (1:2) Zn Ca (1:1) Zn Ca (1:1.5) compositions are acceptable.

Therefore the ratio between Z/Ca should not 1:1.5 exceed and in case of Zn/Ba it should not exceed 1:2.

Table-3. Stabilizers based on linseed oil in the absence of plasticizer
The samples were kept 15 minutes on each temperature

No.	Compositions Zn	Ba	Colours at 150°C	160°C	170°C	180°C
1	3	2:1	Light brown	Brownish	Brown	Black
2	5	1.5:1	Whitish brown	Whitish brown	Light brown	Black
3	1	1:1	Whitish brown	Whitish brown	Light brown	Black
4	4	1:1.5	Off white	Light brown	Yellow	Black
5	2	1:2	Off white	Whitish brown	Light brown	Black
	Zn	Ca				
6	8	2:1	Whitish brown	Pinkish	Pale	Black
7	10	1.5:1	Off white	Off white	Whitish brown	Black
8	6	1:1	Pale yellow	Pinkish	Pale	Black
9	9	1:1.5	Whitish brown	Pale	Pale	Black
10	7	1:2	Whitish brown	Pinkish	Brownish pale	Black
11	11	Reference	Creamy	Cream	Pinkish cream	Black

Preference: Zn Ba (1:1.5) Zn Ca (1:1) Zn Ca (2:1) Zn Ca (1:1.5) Compositions are acceptable.

Table-4. Stabilizers based on sunflower oil in the absence of plasticizer
The samples were kept 15 minutes on each temperature

No.	Compositions Zn	Ba	Colours at 150°C	160°C	170°C	180°C
1	3	1:1.5	White	Off white	Dirty white	Black
2	5	1.5:1	White	Off white	Greyish yellow	Black
3	1	1:1	Off white	Light pale	Pale yellow	Black
4	4	1:1.5	Light yellow	Dark yellow	Brownish yellow	Black
5	2	1:2	Off white	Light pale	Pale yellow	Black
	Zn	Ca				
6	8	2:1	White	Dirty white	Cream	Black
7	10	1.5:1	Light pale	Yellow	Deep yellow	Black
8	6	1:1	Light pale	Pale yellow	Yellow	Black
9	9	1:1.5	White	Dirty white	Cream	Black
10	7	1:2	Off white	Light pale	Dirty pale yellow	Black
11	11	Reference	Creamy	Cream	Pinkish cream	Black

Preference: Zn Ba 1:1, Zn Ba 1:1.5, Zn Ba 1.5:1, Zn Ca 1:2, Zn Ca 2:1, Zn Ca 1:1.5 Compositions are acceptable.

DISCUSSION

Barium, cadmium salts of fatty acid along with or without zinc work as good stabilizer for PVC. Due to the carcinogenic nature of cadmium, its salts were not used in these studies. Calcium and zinc metals are in the list of essential trace metals required by the human body. So calcium and zinc based stabilizers can go for food packaging and in pharmaceutical applications. In these studies Ca/Zn based stabilizers showed their thermal stabilization quality. zinc/barium based stabilizers did not show encouraging results because different metallic salt combinations have different thermal stabilization powers. Specific ratios in the metallic salts play an important role for thermal stability. When the ratio between Ca/Zn was kept 1:1, 1:2, 1.5:1, they showed very good thermal stabilization property. Calcium and barium laurates in the above mentioned ratio also showed thermal stabilizing quality. Similary Ba/Zn based stabilizer also exhibited good thermal stabilizing power. Stabilizers prepared on the base of linseed oil showed poor thermal stabilizing power (Table-2) while sunflower oil based stabilizers showed very good thermal stabilizing property (Table-4). These results clearly indicate that the nature of fatty acid used for the preparation of stabilizers plays a vital role in the stabilization of PVC.

The co-precipitation of metallic soaps gave stabilizers having synergistic properties. The thermal stabilization power increased considerably in case of co-precipitation of metallic soaps used for the preparation of stabilizers.

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