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## Cadmium-Free Liquid Complex Stabilizers for PVC

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### ABSTRACT

A barium-zinc liquid complex stabilizer and a calcium-zinc liquid complex stabilizer (denoted as BZ-3003 and CZ-4004, respectively) have been prepared. Their main components are new types of asymmetric naphthenates of barium and calcium. The applications of these two stabilizers in flexible PVC products proved that they have excellent processing properties and stabilizing efficiency. The flexible clear PVC agricultural film stabilized by BZ-3003 stabilizer has a life span of one and a half years in continuous use, and the similar film stabilized by CZ-4004 stabilizer can be used in outdoor conditions for one year or more. A proper combination of BZ-3003 and CZ-4004 stabilizers may be used as a rather ideal stabilizing system for the manufacture of permeable PVC leathercloth. Formulations and test data in the mentioned applications are presented.

The stabilization of polyvinyl chloride and the stabilizers for it are interesting objects of study. It is known that barium, cadmium, or zinc soaps of long-chain fatty acids and inorganic lead salts are stabilizers usually used in PVC. As most of them are produced in powder form and thus give rise to dust hazards, some stabilizers of

TABLE 1. The Physical Properties of BZ-3003 and CZ-4004 Stabilizers

Stabilizer	Specific gravity	Viscosity (P)	Flash point °C (open cup)	Refractive index $n_D^{20}$	Appearance
BZ-3003	0.9999	0.63	102	1.4785	Yellowish oily liquid
CZ-4004	0.9910	0.8440	93	1.4828	Yellowish oily liquid

this kind in the form of granules, flakes, and the like were developed. However, they result in a poor dispersion in PVC and result in plate-out and blooming. Moreover, there is a growing public criticism toward using stabilizers containing cadmium. Therefore, in some countries much attention has been directed to research and development of cadmium-free liquid complex stabilizers which have very good compatibility and dispersity in PVC and do not cause powder hazards. With synergistic effects between their components, these stabilizers generally exhibit excellent heat and light stabilizing efficiency.

We have also worked with complex stabilizing systems and succeeded in preparing two types of stabilizers, denoted as BZ-3003 and CZ-4004, respectively. The former is a barium-zinc liquid complex stabilizer and the latter is a calcium-zinc liquid stabilizer. Their physical properties are given in Table 1.

The main components of these two liquid stabilizers are new types of asymmetric naphthenates of barium and calcium, both with yellowish color and good flow properties. The other component, a zinc salt of a fatty acid, is dehydrated by a fluidized extraction process so as to obtain an oily suspension and avoid completely the formation of powder. With an optimum ratio of the metal content of barium-zinc or calcium-zinc, the addition, in proper amounts, of phosphite, epoxide, and substituted phenol promotes the synergistic effect, thus imparting to the stabilizers excellent properties of resistance to heat and light degradation of PVC. A comparison of efficiency of BZ-3003 and CZ-4004 with other related stabilizers is shown in Fig. 1.

The results of using BZ-3003 and CZ-4004 in flexible PVC articles proved that the stabilizers have good processing properties and stabilizing efficiency for transparent products. They are stable in storage and can be stored more than one and a half years without any precipitate. Examples of their actual applications are as follows.

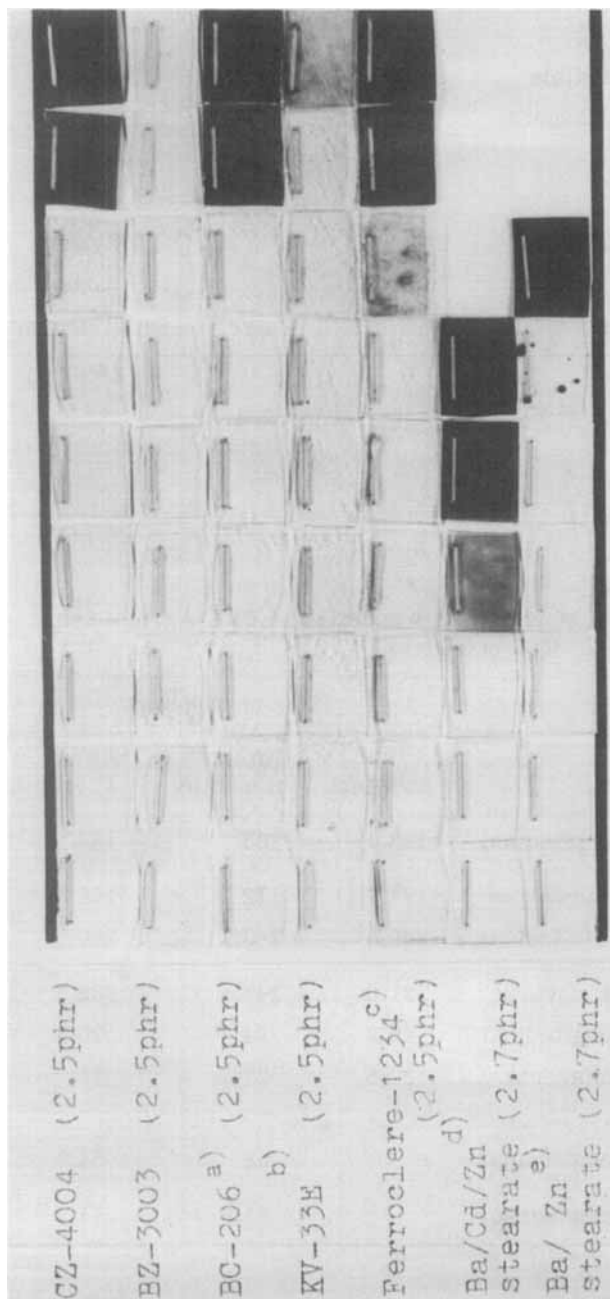


FIG. 1. Comparative efficiency of BZ-3003 and CZ-4004 stabilizers with other liquid and powder form stabilizers in XS-2 suspension PVC (LD65-1 heat test oven, 170°C. Basic test formulation: PVC, 100 parts; dioctyl phthalate, 45 parts; epoxidized ester, 5 parts; stearic acid, 0.5 parts; and stabilizer, 2.5 or 2.7 parts). a) The trade name of a barium-cadmium-zinc liquid complex stabilizer. b) The trade name of a barium-cadmium-zinc liquid complex stabilizer. c) The trade name of a barium-cadmium-zinc liquid complex stabilizer. d) Ingredients: Barium stearate, 1.2 phr; cadmium stearate, 0.8 phr; zinc stearate, 0.2 phr; and phenyl di-isooctyl phosphite, 0.5 phr. e) Ingredients: Barium stearate, 1 phr; zinc stearate, 1 phr, phenyl di-isooctyl phosphite, 0.5 phr; and Bisphenol A, 0.2 phr.

TABLE 2

Suspension PVC (XS-2)	100 parts
Di-(2-ethylhexyl)phthalate	47 parts
Phenyl di-isooctyl phosphite	0.5 parts
Epoxidized ester	3 parts
Stearic acid	0.5 parts
UV absorber (UV-327)	0.3 parts
BZ-3003 stabilizer	3 parts
Phthalocyanine Blue	Small amounts

TABLE 3. Change of Mechanical Properties of PVC Agricultural Film Stabilized by BZ-3003 Stabilizer

Properties		Time of exposure		
		Original	After 8 months	After 17 months
Tensile strength (kg/cm <sup>2</sup> )	Longitudinal	193.1	203	184.5
	Transverse	171.7	172	170.4
Elongation at break (%)	Longitudinal	300.5	249.1	260.7
	Transverse	321.3	244.4	282.5
Elongation at low temperature (%)	Longitudinal	29.5	24.8	20.3
	Transverse	30.5	27.1	22
Right angle tear strength (kg/cm <sup>2</sup> )	Longitudinal		58	54.6
	Transverse		61.6	71.7

TABLE 4

Suspension PVC (XS-2)	100 parts
Di-(2-ethylhexyl)phthalate	42 parts
Diocetyl sebacate	8 parts
Epoxidized ester	3 parts
UV absorber (UV-9)	0.5 parts
Phenyl di-isooctyl phosphite	0.8 parts
Bisphenol A	0.2 parts
Paraffin	0.5 parts
CZ-4004 Stabilizer	3 parts
Phthalocyanine Blue	Small amounts

#### APPLICATION IN PVC AGRICULTURAL FILMS

##### Using BZ-3003 Stabilizer in the Manufacture of Flexible Clear PVC Agricultural Film

The formulation is given in Table 2.

The film is manufactured by calendaring at a temperature of 160-170°C and used as covers for greenhouses for cultivating vegetables in the Beijing area with a life span of one and a half years in continuous use. This shows that the stabilizer is of good performance. Test results are given in Table 3.

##### Using CZ-4004 Stabilizer in the Manufacture of Flexible Clear PVC Agricultural Film

The formulation is given in Table 4.

This film is used for greenhouses in areas of northeast China. Test results are listed in Table 5.

These data show that the film has a life span of one year or more when it is in outdoor use in a cold area, and the stabilizer used can meet this requirement satisfactorily.

#### APPLICATION IN THE MANUFACTURE OF PERMEABLE PVC LEATHER CLOTH

The formulation is given in Table 6.

TABLE 5. Change of Physical and Mechanical Properties of PVC Agricultural Film Stabilized by CZ-4004 Stabilizer

Properties	Time of exposure					
	Original	After 3 months	After 6 months	After 9 months	After 12 months	
Tensile strength (kg/cm <sup>2</sup> )	Longitudinal	258	225	228	276	254
	Transverse	164	146	165	169	169
Elongation at break (%)	Longitudinal	255	275	263	219	233
	Transverse	299	250	245	215	238
Right angle tear strength (kg/cm <sup>2</sup> )	Longitudinal	90	92	97	103	
	Transverse	73	85	99	95	
Elongation at low temperature (%)		28.5	22	19.5	11.5	11.5
Loss on heating (%)		0.91	0.58	0.39	0.41	
Water extract (%)		0.64	0.11	0.05	0.044	

TABLE 6

PVC	100 parts
Di-(2-ethylhexyl)phthalate	72 parts
Permeable blowing agent (BHK-1)	7 parts
Pigment paste	16.5 parts
BZ-3003 Stabilizer	2 parts

TABLE 7. Effect of BZ-3003/CZ-4004 Ratio on Permeability

BZ-3003:CZ-4004	Permeability (mL/cm <sup>2</sup> ·h)	Expansion (%)
1:1	3100	353
1:2	7000	298

The end products proved that BZ-3003 is quite suitable for the manufacture of permeable PVC leather cloth. Its dispersion in PVC resin is much better than that of solid stabilizers, and it is very helpful in promoting the efficiency of the blowing agent on account of its high zinc content, thus giving the product a better expansion. If there is a proper amount of CZ-4004 stabilizer added to the formulation, the permeability of PVC leather cloth will be considerably improved. Some test data are given in Table 7.

In general, BZ-3003 stabilizer is advantageous to the expansion and CZ-4004 to the permeability, both assuring a uniform blowing. Therefore, for some specific flexible PVC products such as permeable leathercloth, a combination of these two stabilizers may be considered as a rather ideal stabilizing system in practical use.