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Thiol-s-triazine as a Stabilizer for Thermal Discoloration

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Thiol-s-triazine as a Stabilizer for Thermal Discoloration

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ABSTRACT

The formation of longer polyene chains (thermal discoloration) has been found to be avoidable by using thiol-s-triazines, such as 2-anilino-4,6-dithiol-s-triazine (AF), which hardly reacts with the original chlorine atoms but tends to replace the activated chlorine (allylic chloride) that plays an important role in triggering zipperlike dehydrochlorination. The optimum stabilizing system is: PVC, 100; DOP, 50; AF, 0.18; Zn stearate, 0.5; Ba stearate, 1.5 parts.

As mentioned in an earlier paper [1], derivatives of dithiol-s-triazine have given a crosslinked PVC having excellent stability for a thermal coloration. In this discussion, I would like to present some properties of thiol-s-triazine as a stabilizer for thermal discoloration of PVC.

2-R-4,6-dithiol-s-triazine shows a different degree of reactivity to PVC, depending on the acidity of thiol group and the basicity of the acid acceptor [1]. Accordingly, the formation of longer polyene chains may be avoided, by using thiol-s-triazine, which never reacts with the original chlorine atoms but tends to replace the activated chlorine (allylic chloride) that plays an important role in triggering zipperlike dehydrochlorination. Really, less reactive thiotriazines, such as 2-anilino-4,6-dithiol-s-triazine (AF) which hardly reacts as a crosslinking agent on PVC, have been confirmed to bond chemically

TABLE 1. Relation between Reactivity of Thiol Group and Stabilizing Activity of 2-R-4,6-Dithiol-s-triazines[a]

	Control	$(C_4H_9)_2$		NHC_6H_5	OC_4H_9
pK_α of thiol group	-	4.5	5.3	5.4	5.8
Period of time when gel formation becomes detectable at 180°C (min)	60	10	60	50	70
Period of time (min) the sample remains colorless at 180°C (min)	<10	10	10	20	20
Chemically bonded thiol triazine (mmole/100 g PVC)[b]	0	4.83	-	0.37	-

[a]Common recipes: Zeon 101 EP, 100 parts; DOP, 50 phr; Ca stearate, 0.5 phr; MgO, 1 phr; 2-R-4,6-dithiol-s-triazine, 0.2 phr.

[b]Recipe: Zeon 101 EP, 100 parts; DOP, 50 phr; MgO, 1 phr; 2-R-4,6-dithiol-s-triazine calcium, 1.5 phr; 180°C, 30 min.

TABLE 2. Stabilizing Effect of Thiol-s-triazine Derivatives on the Coloration of Uncrosslinked PVC

Recipes	Control 1	No. 1	No. 2	Control 2	No. 3	No. 4	No. 5
Geon 101 EP (parts)	100	100	100	100	100	100	
DOP (phr)	40	40	40	-	-	-	-
Reofos 65 (phosphate type) (phr)	-	-	-	50	50	50	50
Ba stearate (phr)	3	3	2	3	3	2	2
Ca stearate (phr)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Zn stearate (phr)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MgO (phr)	2	2	1.5	3	3	2	-
CaO (phr)	1	1	1.5	-	-	1	2
ZnO (phr)			0.07				-
SnO_2(phr)							0.5
Thioltriazine derivative (phr)[a]	-	1 (T_1)	0.2 (T_2)	-	1 (T_1)	T_2: 0.7 T_3: 0.5	T_4: 0.5
Phosphite type chelator (Mark C) (phr)	1	1	1	1	1	1	1
Time samples remain colorless at 180°C (min)	30	>250	130	15	120	60	130

[a] T_1: dibutyltin-thio-s-triazine, T_2: 2-anilino-4,6-dithiol-s-triazine(AF)-Ba, T_3: 2-dibutylamino-4, 6-dithiol-s-triazine(DB)-Ba, T_4: AF.

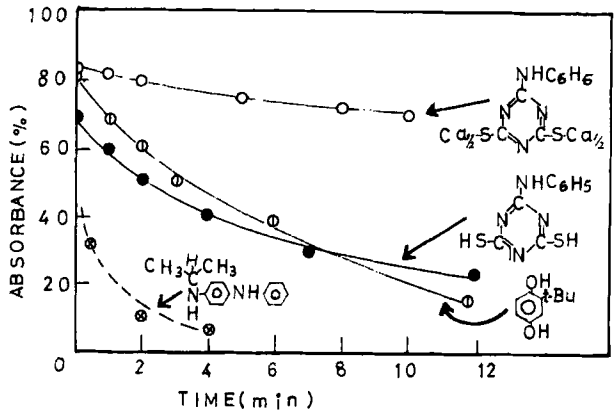

FIG. 1. DPPH radical-accepting behavior of thiol-s-triazine showing a decrease of absorbance (515 nm) of 1 mM DPPH/CH_3OH with equimolar amounts of acceptor at 7°C.

with PVC to show a remarkable stabilizing effect for a discoloration. Comparing with control PVC (Table 1), much less dehydrochlorination is observed in the PVC compounds containing AF. Therefore, the formation of longer polyene chain which causes the discoloration of PVC has been found to be avoidable through AF-MgO system which readily removes the hydrogen chloride, and substitutes allylic chloride with thiolate anion.

The optimum stabilizing system selected in the present work is a combination of AF with organic tin compounds or alkaline earth oxides and some stearate. The system inhibits the discoloration further in the presence of Ca, Ba, and Zn stearates, which show the property of complementary coloring. Such a system is found to increase the color stability of PVC up to around two times that with a conventional stabilizer as shown in Table 2 [1]. As presumed on the radical accepting reactivity of AF with 1,1-diphenyl-2-picrylhydrazyl (Fig. 1), AF is also assumed to stabilize the free radical that accelerates the decomposition of PVC and then to inhibit the discoloration. Such an action is not observed with the commonly used metal stearates. In addition, the stabilizing system with AF was found to be quite effective for PVC blends containing incombustible plasticizers such as tricresyl phosphate and substituted phenyl phosphates, which are inferior to dioctyl phthalate in color stability.

REFERENCES

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