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New Poly(vinyl Chloride) Stabilizers: Epoxidized Novolak Resins

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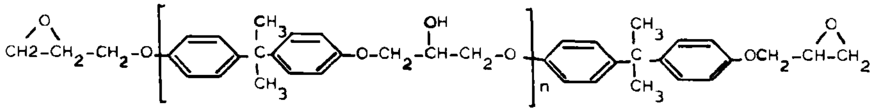
ABSTRACT

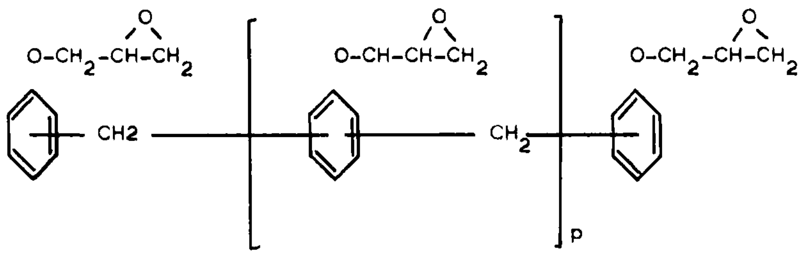
Phenol-formol prepolymers (novolak resins) fully epoxidized, with a molecular weight around 1000, can be mixed with other powdered compounds in stabilization formulation for poly(vinyl) chloride). They can replace epoxidized soyabean oil, with improvement of the Vicat softening point of rigid fabrics. A number of examples are given.

Epoxidized derivatives have been used for many years as PVC stabilizers because of the high reactivity of the epoxy group with HCl. The first type of epoxy product (phenoxypropene oxide) was used in 1932 by I. G. Farben Industries but showed too high a volatility. Other aliphatic or aromatic derivatives with a linear or cyclic structure have been epoxidized and are used as PVC stabilizers. If linear products are relatively low viscous liquids such as epoxidized soybean oil, the cyclic derivatives, and more particularly aromatics, are rather viscous liquids or soft solids which are very hard to handle.

If we look at the formulation of diphenylolpropane epoxidized resins, the molecule contains two epoxy groups. As a matter of fact, these resins must have an epoxy equivalent weight of about 200 to have a good efficiency. Above this value, we know by experience



that the stabilizing efficiency decreases very quickly. If N = 0, the epoxy equivalent weight is 340/2 = 170. This compound is the diphenylolpropane diglycidyl ether which is extremely viscous and very hard to handle. When $n > 0$, the stabilizing efficiency decreases very quickly. Epoxidized novolak resins have not this disadvantage; as a matter of fact, all the OH phenolic groups in the molecule can be epoxidized, and we have one epoxy function per aromatic ring.



The epoxy equivalent weight is $(312 + 162p)/(p + 2) \simeq 162(p+2)/(p + 2) = 162$, whatever p may be.

If the molecular weight of the phenolic resin is high enough (about 1000) these resins are solid lumps which can easily be ground and can be then mixed with the other powdered compounds used in a stabilization formulation. It is difficult to obtain a fully epoxidized resin when the molecular weight is high. It is however, possible. Compared to the epoxidized soybean oil usually used, these novolaks have a greater efficiency (3 parts of soybean oil derivative can be replaced by 1 or 2 parts of the resin), and they do not modify the Vicat softening point in rigid PVC.

In a standard formulation for bottles, we obtain the following results: 3 parts of ESO, giving a Vicat point of 74°C, could be replaced by 1 part of epoxy novolak and the Vicat softening point is 80°C. Some very interesting results were obtained in the following fields: bottles, profiles and rigid sheets, rigid pipes and also plasticized PVC, vinyl asbestos tiles, and chlorinated poly(vinyl chlorides). However, toxicity is an important property when health hazard is involved.

Epoxidized phenolic resins polymerized with a nontoxic hardener are widely used for metallic can coatings. The resins crosslink and have a very high molecular weight. There are, however, some rather low molecular weight products. The molecular distribution measured

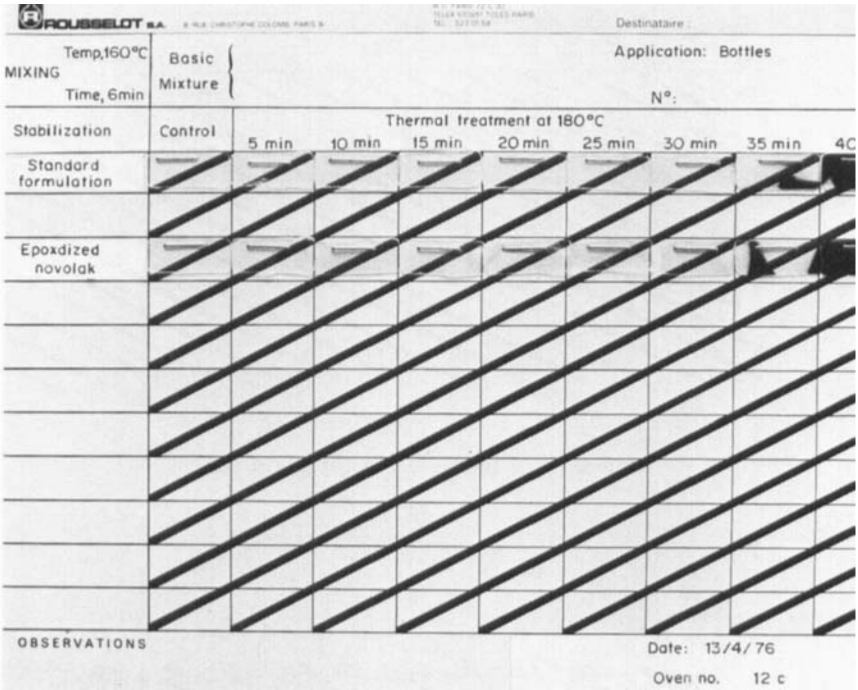


FIG. 1. Performance of formulation for bottles.

by gel-permeation chromatography is not very precise but shows that we have some molecular weights lower than 100. It is therefore necessary to run technological tests on each type of resin which can be used in this application. The first tests, with rats, showed that by oral adsorption these resins had no lethal effect at 10 g/kg.

In some formulations we found some initial yellowing of the PVC, similar to that obtained when phenolic antioxidants are used. We can avoid this phenomenon by modifying the formulation (Zn, various additives) if the content of epoxidized resin is not too high. These products have a limited compatibility with PVC, but sufficient to obtain a good efficiency in rigid crystalline PVC. When plasticized PVC is concerned, compatibility with plasticizers is also limited: it is better with DBP than with DOP.

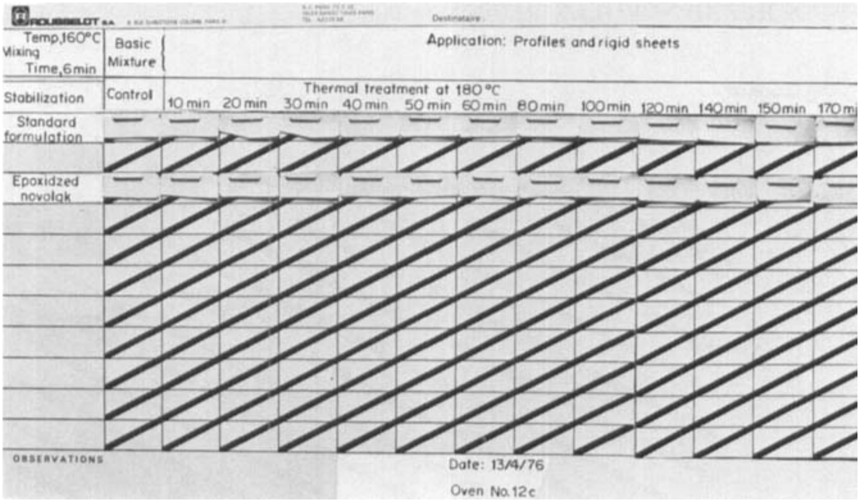


FIG. 2. Performance of formulation for rigid sheets.

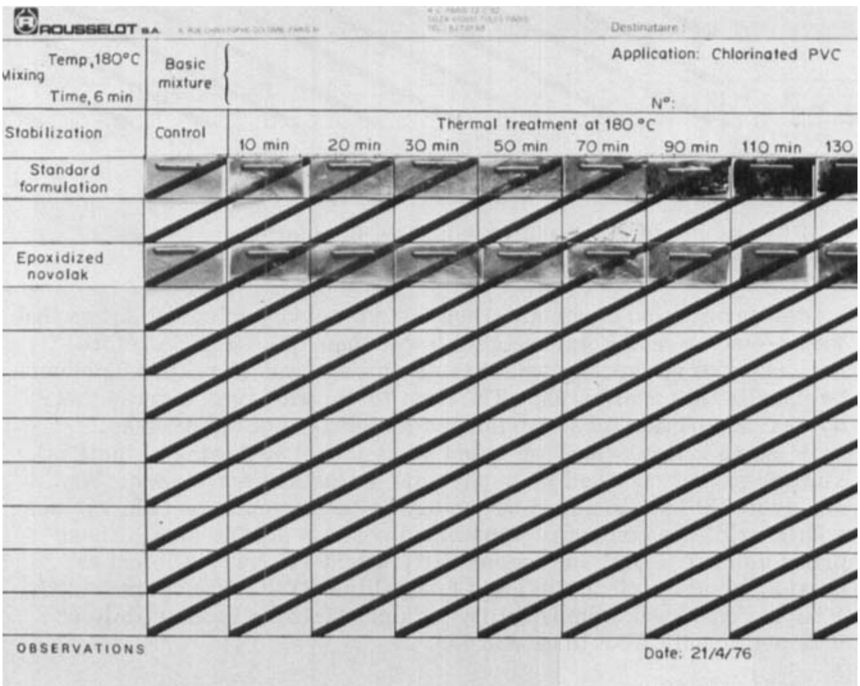


FIG. 3. Performance of chlorinated PVC formulation.

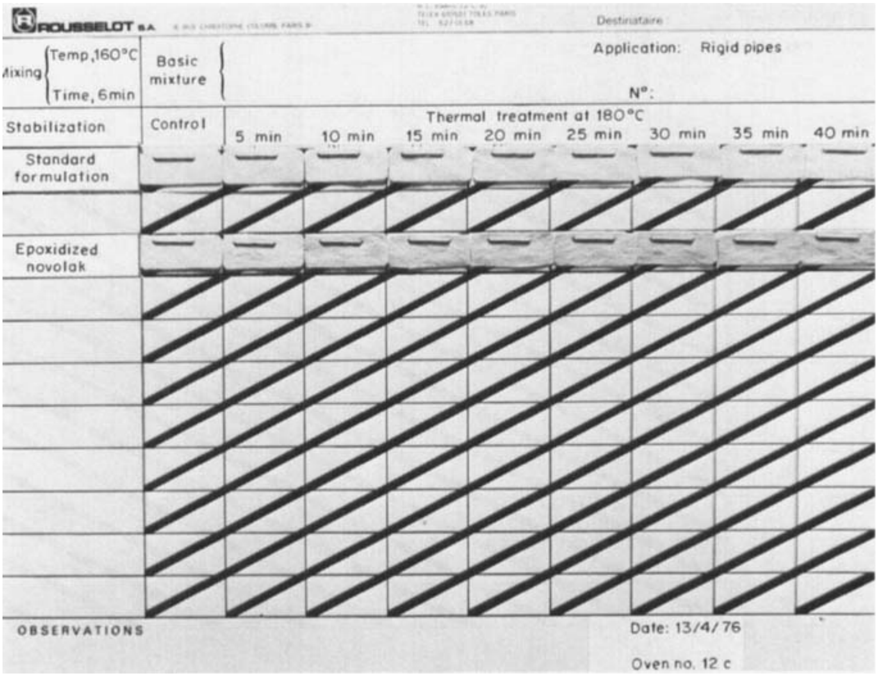


FIG. 4. Performance of formulation for rigid pipes.

TYPICAL FORMULATIONS

Bottles

A typical formulation for bottles is: PVC, 100 parts; impact modifier, 10 parts; α-phenylindole, 0.25 part; TNPP, 0.5 part; Ca stearate, 0.5 part; Zn octoate, 0.2 part; epoxidized soya oil (ESO), 4 parts. When we replaced 3 parts ESO in this formulation by 0.5 part of epoxidized novolak, stabilization was unchanged; the Vicat softening point rose by about 6°C (Fig. 1).

Profiles and Rigid Sheets

For rigid sheets, a typical formulation is copolymer resin, 100 parts; titanium dioxide, 3 parts; $CaCO_3$, 10 parts; anti-UV compound, 0.2 part; Ba/Cd stabilizer, 1.8 parts; phosphite, 0.5 part; lubricant, 0.3 part; ESO, 1.2 parts. ESO can be replaced by 0.8% epoxidized novolak. Thermal and light stabilities are not modified (Fig. 2).

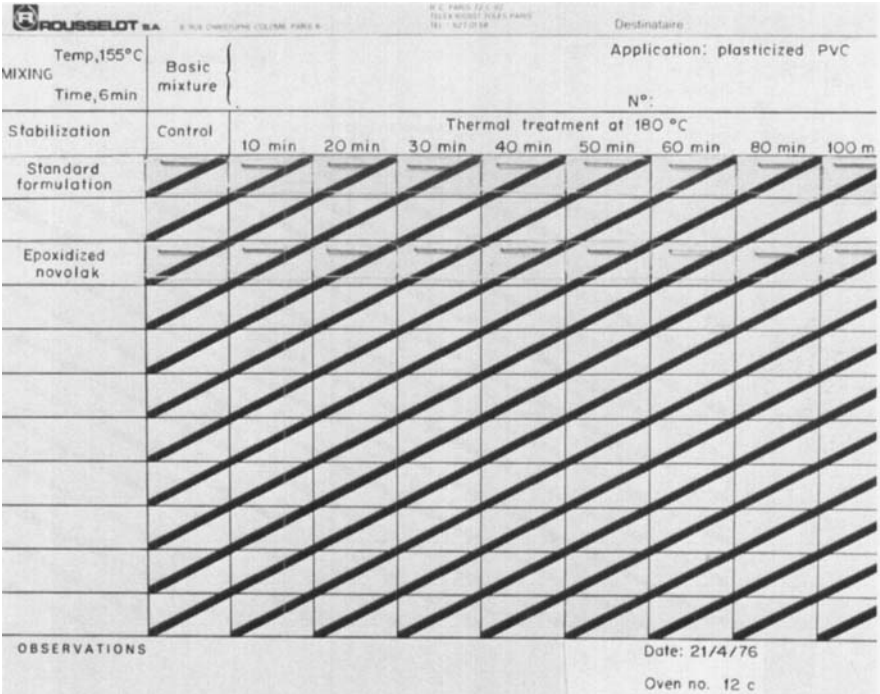


FIG. 5. Performance of plasticized PVC formulation.

Chlorinated PVC

In this type of formulation, ESO cannot be used because it lowers the Vicat softening point too much. We used, with very good results, the following formulation: chlorinated PVC, 100 parts; Ba/Cd stabilizers, 2.5 parts; epoxidized novolak, 2 parts; lubricant, as desired. (Fig. 3).

Rigid Pipes

For nontoxicological purposes, lead stabilizers must be replaced in pipe formulations; for clear pipes, we need good light stability which cannot be obtained with α-phenylindole and Ca/Zn stabilizers. We obtained some interesting results with the following formulation: PVC resin, 100 parts; titanium dioxide, 2 parts; Ca/Zn stabilizer, 1.2 parts; epoxidized novolak, 0.4 part. We can add also diphenylthiourea, (0.05 part) and butylhydroxyanisole (0.1 part) to prevent yellowing (Fig. 4).

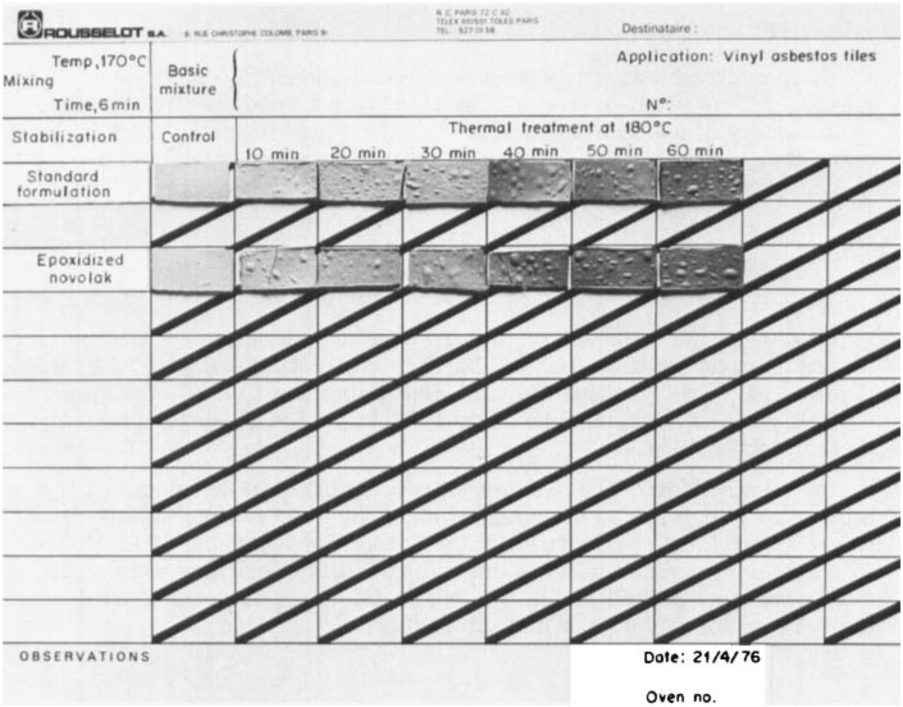


FIG. 6. Performance of formulation for vinyl-asbestos tiles.

Plasticized PVC

In the following formulation: PVC, 72 parts; DOP, 25 parts; lubricant 0.2 part; powdered Ba/Cd stabilizer, 1 part; DPDP, 0.3 part; ESO, 1.5 parts. We could replace DPDP and ESO by epoxidized novolak (0.4 part) and polymer phosphite (0.2 part) (Fig. 5).

Vinyl Asbestos Tiles

For a formulation consisting of vinyl chloride-vinyl acetate copolymer, 100 parts, asbestos, 100 parts; limestone, 250 parts; titanium dioxide, 50 parts; dicyandiamide, 3 parts, we tested two stabilizing systems: $CaCO_3$ (2 parts) plus ESO (2 parts) or epoxidized novolak (1 part). With both systems we obtained the same heat and light stability; water absorption is much lower with the formulation containing the epoxidized novolak (Fig. 6). The epoxidized novolak can be preblended with dicyandiamide.

CONCLUSION

Of epoxidized derivatives used as PVC stabilizers, epoxidized novolak resins seem of interest, as they have a good efficiency in a wide variety of applications and modify the Vicat softening point less than other products. As they can be ground to a fine powder, they are easy to combine with most of the solid PVC stabilizers.

DISCUSSION

Dr. Jungk (Metallgesellschaften, Frankfurt, Germany): Let me please ask you a question about the very interesting stabilizer systems that you have just proposed to us. Most important to me is the compatibility of the novolaks with rigid PVC. Could you please comment on that subject?

Dr. Bicart-See: The problem of compatibility is dependent on the molecular weight. The molecular weight must not be too high in order to get a satisfactory compatibility. A good range is about 1000-10,000. For higher molecular weights the compatibility decreases very much. For lower molecular weights, the products cannot be ground and then they are no longer of practical interest.