

N*-Chloro and *N*-Nitroso Compounds as Synergists for the Self-Extinguishing Action of Bromine Compounds in Polystyrene

ALVIN R. INGRAM, *Research Center, Koppers Company, Inc.,
Monroeville, Pennsylvania*

Synopsis

Compounds other than peroxides may be used to enhance the self-extinguishing action of organic bromine compounds on polystyrene. The addition of certain chloramides or nitrosoamines converts some bromide-containing polystyrene compositions from flammable to instantly self-extinguishing. Two effective chloramides were *N,N*-dichlorotoluene sulfonamide or *N,N'*-dichloro-*N,N'*-diphenyl urea but they were of limited value because of hydrolysis by atmospheric moisture. The more effective nitrosoamines were *N*-nitroso-*N*-methylaniline, *N*-nitrosocarbazole and *N*-nitroso-diphenylamine. An undesirable characteristic of the three compounds is their inhibition of polymerization of styrene. The interaction of a nitrosoamine and an aliphatic bromine compound is apparent from the evolution of nitrogen, nitric oxide, and nitrous oxide. If the minimum temperature for gas evolution falls in the range of about 145–180°C. in a prescribed simple test, the nitrosoamine and bromine compound may be used for rendering polystyrene self-extinguishing.

INTRODUCTION

Bromine compounds are recognized as practical self-extinguishing (SE) agents for hydrocarbons, particularly for fuels¹ and for polystyrene foams.^{2,3} In comparison with their chlorine analogs, the bromine compounds are much more effective. However, the nature of the carbon-bromine bond does play an important role in the efficiency of a bromine compound as a self-extinguishing agent for polystyrene. In particular, the aliphatic bromine compounds are much more effective than the aromatic bromine compounds.² This phenomenon is no doubt associated with the higher carbon-bromine bond strength imparted by the resonance stabilization with the benzene ring. However, even among the aliphatic bromine compounds there is a considerable difference in performance in extinguishing flaming polystyrene. Thus, some aliphatic bromides may be undesirable because they are either too unstable or too stable, decomposing either too far below or above the ignition temperature of polystyrene. Price and

* Presented before the Symposium on Self-Extinguishing Plastics in the Organic Coatings and Plastics Chemistry Division at the 144th Meeting of the American Chemical Society, Los Angeles, March 31–April 5, 1963.

Roche⁴ have shown that the effectiveness of unsymmetrical vicinal dibromides is related to the rate of addition of bromine to the parent olefin. In this case the good self-extinguishing agents are formed within a defined range of rate of bromination.

An important observation in this field was made by Eichhorn and associates,⁵ who found that peroxides were powerful synergists for attaining superior self-extinguishing results from bromides in polystyrene. Thus one can reduce the minimum bromine content by at least one-half by adding only "catalytic amounts" of certain peroxides. This finding also clarified anomalous experimental results which may be attributed to residual peroxides in polystyrene.

It was of interest to examine some thermally unstable compounds other than peroxides to see if they might perform in a similar manner. This investigation was concerned with a study of organic nitrogen compounds in which a chloro or nitroso group is attached to the nitrogen.

Experimental

Screening tests were carried out with dry castings from solutions of polystyrene in methyl chloride. Experimentally, a circular polyethylene bowl of 3-in. bottom diameter was charged with the additive, 5 g. of polystyrene foam particles, and 20 ml. of methyl chloride. It was often convenient to charge the additives from a stock solution in acetone or pentane. In this case, it was necessary to charge the stock solution first and allow the solvent to evaporate because of the difficulty of removing traces of acetone or pentane from the castings. Polystyrene foam particles were used because they dissolved rapidly. In the air stream of a fume hood, the castings hardened

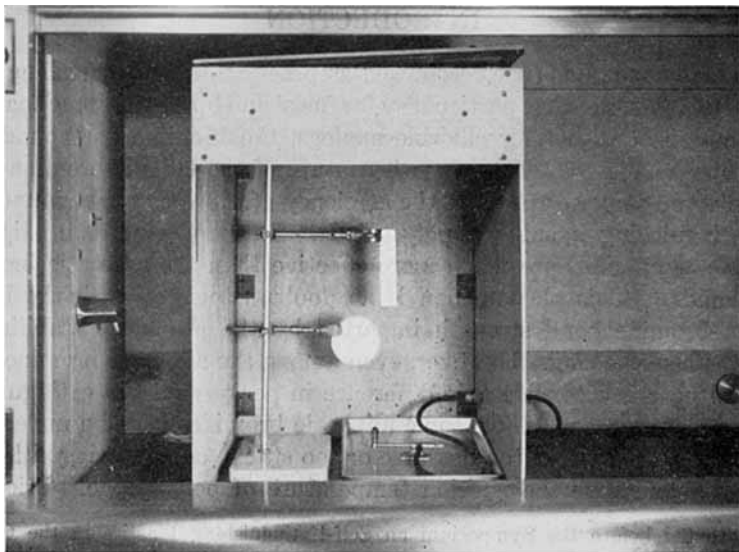


Fig. 1. Specimens in place for self-extinguishing test.

within 1/2-1 hr. They were either stored overnight in an air stream or placed in a vacuum oven at 60°C. for 3-4 hr. before testing. The platelike specimens of dense irregular foam, mounted in a vertical plane through the edge, were contacted for 3 sec. with a 1/2-in. yellow flame of a microburner. The time for the flame to be extinguished was measured by a stop-watch.

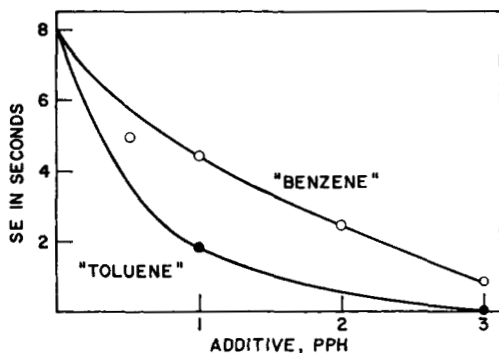


Fig. 2. *N,N*-Dichloroaromatic sulfonamides with 1% $\text{CHBr}_2\text{CBr}_3$.

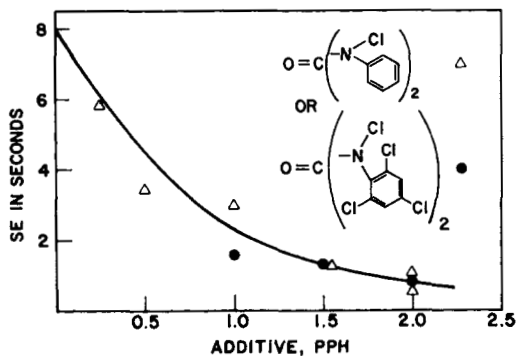


Fig. 3. Chloroureas with 1% $\text{CHBr}_2\text{CBr}_3$.

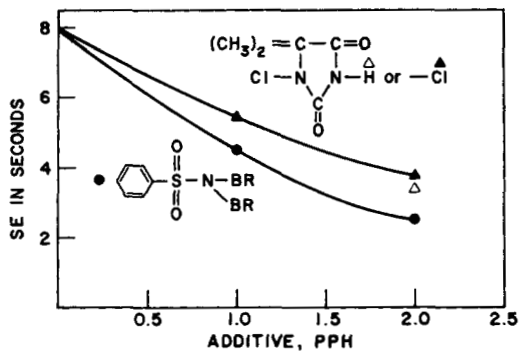


Fig. 4. Other *N*-halo compounds with $\text{CHBr}_2\text{CBr}_3$.

Any specimen burning more than 15 seconds was extinguished by blowing and was considered not self-extinguishing. Self-extinguishing specimens were rotated to present a fresh surface for each ignition.

Any compounds which appeared of promise in the preliminary test were then evaluated in polystyrene foams prepared by the expandable bead method, wherein the additive was incorporated either before or after the polymerization step. The foams were molded at densities of 2-3 pcf.

In Figure 1 are shown specimens mounted for test. There is one casting and one bead foam, the latter trimmed to $5 \times 1 \times \frac{1}{2}$ in. The micro-burner and a tray for catching drips are also included in the picture. A hood within a hood was constructed for this test. The small hood has a glass-fiber filter near the top which retains most of the soot generated. The small hood is constructed of asbestos board and has a hinged top for intermittent removal of fumes by the suction of the main hood. Because of safety regulations it was not permissible to shut off the suction during the test. The tests were not seriously disturbed by drafts in this particular arrangement.

In Figure 2 are given the results of self-extinguishability tests on castings containing 1% pentabromoethane and various amounts of *N,N*-dichlorobenzene sulfonamide and *N,N*-dichlorotoluene sulfonamide. The toluene sulfonamide was superior to the benzene sulfonamide compound. The ordinate represents the average of five self-extinguishability determinations. Pentabromoethane was chosen because it is a convenient solid to handle and because in a concentration of 1-1.25% it was borderline in self-extinguishing action, with an average self-extinguishing time of about 8 sec. Thus, the effect of a synergist was readily recognized and reasonably reproducible. It should be pointed out that when the self-extinguishing time increased beyond about 3 sec., the reproducibility of the self-extinguishing time was rather poor. However, the reproducibility of results at a time of 3 sec. or less was quite satisfactory. For practical purposes, a self-extinguishing time of less than 2 sec. is desired.

In Figure 3 are presented the self-extinguishability results for the best of the *N*-chlorocarbonamides tested: the symmetrical dichlorodiphenylureas.

Figure 4 depicts the effects of three other *N*-halo amides: the mono- and dichlorodimethylhydantoin and *N,N*-dibromobenzene sulfonamide. The curve for the *N,N*-dibromobenzene sulfonamide is similar to that obtained with the *N,N*-dichlorobenzene sulfonamide.

In Figure 5 are given the effects of some *N*-halo compounds (including dichlorodimethylhydantoin) on a different bromine compound, tris(2,3-dibromopropyl) phosphate, which at 2% was not a self-extinguishing agent in this test. It is seen that *N*-bromosuccinimide (NBS) is much more effective than the corresponding chloro compound, *N*-chlorosuccinimide (NCS). However, the two bleaching agents, dichlorodimethylhydantoin (DCDMH) and to some extent dichloroisocyanuric acid (DCICA), were more effective in imparting self-extinguishability than was additional tris(2,3-dibromopropyl) phosphate (T23P). It should be pointed out at this

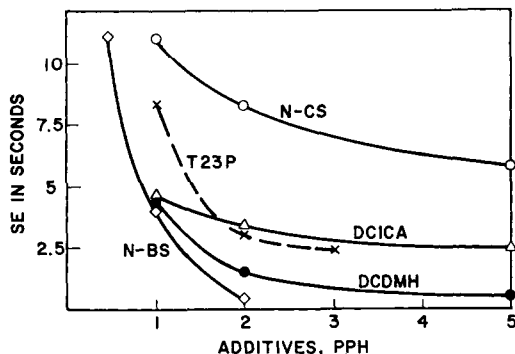


Fig. 5. *N*-Haloamides with 2% $(\text{CH}_2\text{BrCHBrCH}_2)_3\text{PO}_4$.

time that none of the *N*-chloro compounds tested was a self-extinguishing agent *per se* at relatively high concentrations (5%), even in the presence of peroxide.

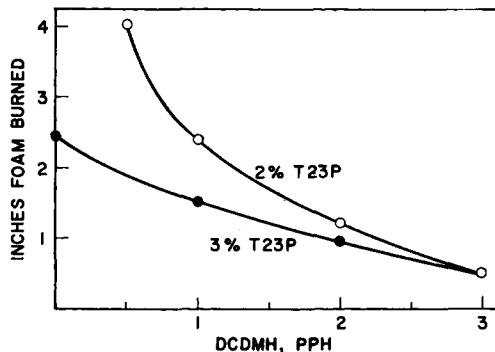


Fig. 6. Foams via DCDMH in monomer.

Because DCDMH showed fairly good hydrolytic stability, an attempt was made (Fig. 6) to prepare foams by the expandable bead technique whereby the bromine compound (T23P) and the synergist (DCDMH) were added to the monomer and the solution was polymerized in suspension. It is seen that the synergist effect was well demonstrated. In this case the ordinate represents the inches of 2 pcf. foam burned vertically. If less than 1.25 in. of foam is destroyed, the product is considered satisfactorily self-extinguishing. In these experiments the polymer became quite brittle with increasing concentration of DCDMH, and an objectionable quantity of hydrochloric acid was generated during the polymerization.

The tendency of the *N*-chloro compounds to hydrolyze, especially at high temperatures, led to a search for other nitrogen derivatives which might generate free radicals on heating. Interest was drawn to *N*-nitroso derivatives, because they have been used as nitrogen-releasing blowing agents (for example, *N,N'*-dinitroso-*N,N'*-dimethylterephthalamide and dinitro-

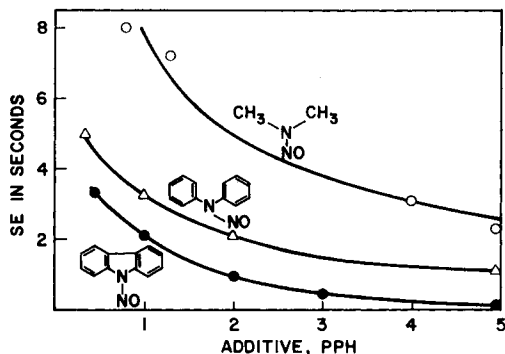


Fig. 7. *N*-Nitroso *sec*-amines with 1% $\text{CHBr}_2\text{CBr}_3$.

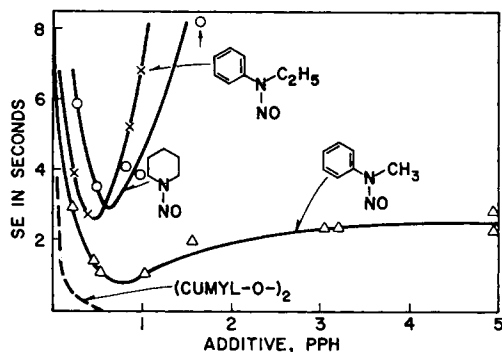


Fig. 8. *N*-Nitroso *sec*-amines with 1% $\text{CHBr}_2\text{CBr}_3$.

sopentamethylenetetramine). Furthermore, these compounds are not readily hydrolyzed.

Figure 7 shows the effects of the *N*-nitroso derivatives of carbazole, diphenylamine, and dimethylamine on the self-extinguishing action of 1% of pentabromoethane. *N*-Nitrosocarbazole was particularly effective. If not for the fact that it is an odorous yellow dye, it might be useful. It is observed that the shapes of these curves are similar to those of the effective *N*-chloro compounds in that the self-extinguishing action improves with increasing concentration of synergist. However, in Fig. 8 it is seen that there are some *N*-nitroso compounds such as *N*-nitrosopiperidine and *N*-nitroso-*N*-ethylaniline which are self-extinguishing synergists at low concentration and then act like fuels at higher concentration in the presence of 1% of pentabromoethane. *N*-Nitroso-*N*-methylaniline exhibits a curve which is intermediate between those of the previous figure and those which show a sharp optimum concentration. *N*-Nitroso-*N*-methylaniline was the most effective nitroso compound at low concentration. In Figure 8, also, this action is compared with a typical peroxy synergist, dicumyl peroxide, which at 0.6% makes the specimen nonignitable in this test. At 0.6% of *N*-nitroso-*N*-methylaniline, the self-extinguishing time averaged 1 sec. A

nonignitable specimen was previously observed (Fig. 7) when 4–5% of *N*-nitrosocarbazole was used as the synergist. Self-extinguishability tests for Figures 7 and 8 were performed with castings. Because the latter two nitroso compounds inhibited the polymerization of styrene, it was not possible to prepare expandable beads therefrom by addition to the monomer. However, self-extinguishing foams were prepared from beads to which *N*-nitroso-*N*-methylaniline was added as a solution in the blowing agent.

To determine if the self-extinguishing action might be due to the nitroso group alone, a number of other classes of compounds were tested; some ineffective nitrogen oxides are listed in Table I. The first example is a particularly good one because it illustrates the effect of removing the nitroso group from the nitrogen position of a good synergist (*N*-nitrosodiphenylamine) to the *para* position where there is no synergistic action. Other ineffective materials were *N*-oxides (pyridine and picoline), *N*-nitrosocarboxylic amides, *N*-nitroso-sulfonic amides, and the azoxy. However, as seen in the second part of Table I, one cannot generalize that all *N*-nitroso secondary amines are synergists. It is surprising that the first compound is ineffective because it is merely the *p*-nitroso derivative of the excellent

TABLE I
Ineffective Nitrogen Oxides and *N*-Nitroso-*sec*-amines

	Structure
Ineffective nitrogen oxides	
Aromatic nitroso	
<i>N</i> -Oxide	
<i>N</i> -Nitroso-C-amide	
<i>N</i> -Nitroso-S-amide	
Azoxy	
Ineffective <i>N</i> -nitroso- <i>sec</i> -amines	
<i>p</i> -Nitroso- <i>N</i> -nitroso- <i>N</i> -methylaniline	
<i>N</i> -Nitroso- <i>N</i> -benzylaniline	
<i>N,N</i> -Dinitrosopentamethylenetetramine	

synergist, *N*-nitroso-*N*-methylaniline. Also, the second compound (*N*-nitroso-*N*-benzylaniline) is ineffective in spite of the fact that it is so closely related to three active materials: *N*-nitrosodiphenylamine, *N*-nitroso-*N*-methylaniline, and *N*-nitrosodimethylamine. These results suggest that the flame-extinguishing reaction might be dependent on temperature. To test this hypothesis, the temperature was observed at which a gas was generated when solutions of pentabromoethane and various *N*-nitroso compounds in triethylbenzene were heated in capillary melting point tubes. Triethylbenzene was chosen because of its high boiling point, 217–220°C., and because it simulated, to some extent, polystyrene as an environment. Furthermore, neither pentabromoethane nor the *N*-nitroso compounds evolved a gas from solutions in triethylbenzene below the boiling point. The results shown in Table II were obtained by heating solutions containing 5% of pentabromoethane and 9% of the *N*-nitroso compound. The temperature at which gases were evolved correlate very well with the self-extinguishing test, indicating a favorable rapid decomposition range of 145–180°C., or preferably a narrower range of 155–172°C. It is also significant that the instantaneous decomposition temperature of the preferred peroxide synergists are in this same range. At this point it should be pointed out that certain pairs of chlorine compounds and nitrosoamines were found to evolve gases within the preferred range. However, none of these combinations was a self-extinguishing agent.

TABLE II
Reaction of *N*-Nitroso Compounds with $\text{CHBr}_3\text{CBr}_3^a$

<i>N</i> -Nitroso Compound	Gas, °C.	SE
Pentamethylenetetramine	122	None
<i>N</i> -Methyl- <i>p</i> -nitrosoaniline	144	None
<i>N</i> -Benzylaniline	145	None
<i>N</i> -Phenylaniline	155	Good
Carbazole	164	Excellent
<i>N</i> -Methylaniline	172	Excellent
Piperidine	180	Fair
Dimethylamine	210	Poor

^a 9% *N*-NO compound; 5% $\text{CHBr}_3\text{CBr}_3$; 86% tri-ethylbenzene.

Table III shows the gases obtained from a triethylbenzene solution of *N*-nitrosodiphenylamine and pentabromoethane at 155–164°C. The gases were identified in the mass spectrometer. The major product was nitrogen. The minor products were nitric oxide and nitrous oxide, which, being heavier, were concentrated in the reaction vessel rather than downstream in the receiver. The decomposition depicted in Table III was carried out in a dry helium atmosphere. In an air atmosphere with no precautions for dryness, the results were substantially the same, except that the gas was brown, instead of colorless, because of traces of nitrogen dioxide. It was surprising that in none of these tests was there any bromine compound detected in the gas samples.

styrene are formed by attack of bromine atoms or the added bromine-containing self-extinguishing agent. These tentative mechanisms are represented above in eqs. (4) and (5). The bromopolystyrene is most likely a better self-extinguishing agent than the added bromine compound as it is less volatile and because it has a favorable temperature range of releasing hydrogen bromide. As an indirect proof, it is pointed out that polystyrene, brominated in water in the presence of an oxidizing agent, especially potassium persulfate,⁸ had very good self-extinguishing properties at only 1% of combined bromine in the absence of any synergist. Although the evidence is incomplete, it is proposed that the bromine is located mostly in the α,β positions because the brominated polystyrene retarded the thermal polymerization of styrene to the same extent as α,β -dibromoethylbenzene. α -Bromoethylbenzene caused less retardation of polymerization while β -bromoethylbenzene had substantially no effect on the rate.

The author is indebted to Drs. S. Temin and B. Rudner for helpful suggestions and samples, to Dr. E. W. Albaugh and Mr. W. E. McKinstry for gas analyses, to Dr. E. H. Gleason for polymerization rate studies, and to Mr. H. L. Nicholson for performing the self-extinguishing evaluations.

References

1. Burgoyne, J. H., and G. Williams-Leir, *Proc. Roy. Soc. (London)*, **A193**, 525 (1948).
2. McCurdy, J. L., and L. Kin (to The Dow Chemical Company), U.S. Pat. 2,676,927 (April 27, 1954).
3. Buchholz, K., and F. Stastny (to Badische Anilin- and Soda-Fabrik A.G.), U.S. Pat. 3,001,954 (September 26, 1961).
4. Price, R. M., and A. F. Roche (to The Dow Chemical Company), U.S. Pat. 2,723,963 (November 15, 1955).
5. Eichhorn, J. (to The Dow Chemical Company), U.S. Pat. 3,058,926 (October 16, 1962); E. L. McMaster, J. Eichhorn, and F. B. Nagle (to The Dow Chemical Company), U.S. Pat. 3,058,927 (October 16, 1962); J. Eichhorn and S. I. Bates (to The Dow Chemical Company), U.S. Pat. 3,058,928 (October 16, 1962); J. W. Vanderhoff and A. K. Jahn (to The Dow Chemical Company), U.S. Pat. 3,058,929 (October 16, 1962).
6. Rosser, W. A., Jr., S. H. Inami, and H. Wise, WADC Technical Report 59-206, ASTIA Document No. AD 216355, Wright Air Development Center, April 1959.
7. Rosser, W. A., Jr., J. H. Miller, S. H. Inami, and H. Wise, Final Report, Phase II, Stanford Research Institute, June 1958.
8. Ingram, A. R. (to Koppers Company, Inc.), U.S. Pat. 3,039,977 (June 19, 1962).

Résumé

D'autres composés que les peroxydes peuvent être employés pour augmenter l'action auto-extinctive des composés bromés organiques sur le polystyrène. L'addition de certaines chloramides ou nitrosamines transforme certaines compositions de polystyrène contenant du brôme et inflammables en un produit auto-extinctif. Deux chloramides efficaces sont le *N,N*-dichlorotoluène sulfonamide ou la *N,N'*-dichloro-*N,N'*-diphényle urée mais sont d'une valeur limitée à cause de l'hydrolyse par l'humidité atmosphérique. Les nitrosamines les plus efficaces sont la *N*-nitroso-*N*-méthylaniline, le *N*-nitrosocarbazole et la *N*-nitrosodiphénylamine. Une caractéristique indésirable de ces trois composés est leur effet inhibiteur sur la polymérisation du styrène. L'interaction entre une nitrosamine et un composé aliphatique bromé rendue visible par le dégragement d'azote, d'oxyde azotique et d'oxyde azoteux. Si la température minimum pour le dégagement

gazeux tombe dans le domaine d'environ 145–180°C dans un test simple pres crit, la nitrosamine et le composé bromé peuvent être utilisés pour rendre le polystyrène auto-extinctif.

Zusammenfassung

Andere Verbindungen als Peroxyde können zur Erhöhung der selbstlöschenden Wirkung von organischen Bromverbindungen auf Polystyrol verwendet werden. Der Zusatz gewisser Chloramide oder Nitrosoamine wandelt bromidenthaltende Polystyrolmischungen von entflammaren in sofort selbstauslöschende Substanzen um. Zwei wirksame Chloramide sind *N,N*-Dichlortoluolsulfonamid und *N,N'*-Dichlor-*N,N'*-diphenylharnstoff; wegen der Hydrolyse durch atmosphärische Feuchtigkeit besitzen sie aber nur begrenzten Wert. Besser wirksame Nitrosoamine sind *N*-Nitroso-*N*-methylanilin, *N*-Nitrosocarbazol und *N*-Nitrosodiphenylamin. Eine unerwünschte Eigenschaft der drei Verbindungen ist die Verhinderung der Styrolpolymerisation. Die Reaktion zwischen einem Nitrosamin und einer aliphatischen Bromverbindung ist an der Entwicklung von Stickstoff, Stickoxyd und Stickoxydul merklich. Wenn bei einem angegebenen einfachen Test die Mindesttemperatur für die Gasentwicklung in den Bereich von etwa 145–180°C fällt, können das Nitrosamin und die Bromverbindung zur Erzielung der Selbstauslöschungsfähigkeit von Polystyrol verwendet werden.

Received September 23, 1963