Sulfonyl Hydrazide Blowing Agents for Rubber and Plastics

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THE utilization of gas-forming chemicals in the manufacture of expanded rubber has been widely practiced for many years. Their application in the formation of expanded plastics is a more recent development, but a fair sized industry is developing in this field as well. The methods employed make use of the dry polymer. The products are characterized by the initial formation of a closed or discontinuous cell structure, although in some applications the cells are ruptured during or after blow. It is the object of this paper to deal with new gas-forming chemicals for the preparation of unicellular rubber and plastic products.

Sodium bicarbonate, usually employed in conjunction with a fatty acid, has been the most widely used blowing agent in rubber, although it possesses certain disadvantages. In order to obtain fine, uniform cell structure in rubber, it is necessary to effect extremely thorough dispersion of the blowing agent. With sodium bicarbonate and other rubber-insoluble blowing agents this is difficult to accomplish. Better results are obtained with several rubber-compatible organic blowing agents which have been introduced in recent years. During vulcanization these materials decompose smoothly to give a uniform liberation of gas throughout the composition and a fine cell structure is obtained. Examples of two organic materials that have been sold commercially are diazoaminobenzene (*4*) and dinitrosopentamethylenetetramine (*3*). Diazoaminobenzene may cause dermatitis and is limited to applications where discoloration is not an objectionable feature. Dinitrosopentamethylenetetramine may be used in light-colored stocks but produces an undesirable, fishy odor in some applications.

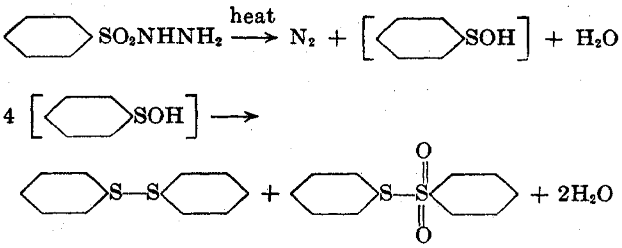
Another organic substance that has been used to a limited extent as a blowing agent is α,α-azobis-(isobutyronitrile). This product, a result of German technology during the recent war, has become known as Porofor N (*7*). It is capable of producing expanded rubber of exceedingly fine cell structure and is free from discoloration. Rubber and plastic foams prepared from this compound have desirable characteristics and considerable interest had been taken in the material for such applications. Unfortunately, a toxic residue is formed during the decomposition of Porofor N, which has retarded its commercial development as a blowing agent. Another disadvantage of the compound is its low blowing temperature which weighed against its addition to plastics on a hot mill. Nevertheless, the blowing characteristics of Porofor N constitute a high standard of excellence, and it has been considered that a chemical which gives these characteristics with no toxicity would approach the ideal blowing agent for rubber and plastics.

The ideal blowing agent will be nondiscoloring and nonstaining and will not produce toxic or odorous residues within the expanded product. Further, it should be easily and thoroughly dispersible in the rubber or plastic and should not affect the stability or the rate of cure of the composition into which it is introduced. It will be stable at normal storage and mixing temperatures but will decompose evenly at practical processing temperatures to produce a gas. Nitrogen is considered to be a preferred blowing gas, not only because it is inert, but also because the permeability of rubber and other polymers to nitrogen is considerably lower than for most other gases (*1*). It may also be of significance that its partial pressure in the atmosphere is higher than that of any other gas.

The techniques of blowing rubber have been well described (*4, 6, 8, 11, 12*). Less information is available concerning the production of blown plastics (*2, 7*). The same basic principles apply to both applications but the methods differ. Both types must be plastic enough to expand under the pressure of the gas and yet strong enough to hold their expanded shapes. With rubber or thermosetting plastics, strength is achieved through vulcanization or cure, which must be carefully balanced with the rate of gas evolution. With thermoplastic resins the same ends may be accomplished by generation of the gas within the resin in confinement under pressure, with subsequent expansion of the plastic at a temperature governed by the strength and plasticity of the resin formulation.

INITIAL STUDIES

The present work started with the discovery that benzenesulfonyl hydrazide gave excellent blow and a fine cell structure in expanded polyvinyl chloride. The compound seemed to meet most of the requirements for an ideal blowing agent but, unfortunately, it also left a foul, mercaptan-like odor in the product. A search of the literature revealed that the decomposition of the compound involved an internal oxidation-reduction of the sulfonyl hydrazide group (*5*). A possible mechanism of the gas-forming reaction has been suggested



(1A)

(1B)

The hypothetical intermediate, benzenesulfenic acid, is apparently incapable of existence and immediately disproportionates to a disulfide and a thiosulfonic ester as indicated in Equation 1B (*9*). The earlier investigators (*5*) succeeded in isolating diphenyl disulfide from the reaction products but did not isolate the thiosulfonic ester (or "disulfoxide" in their nomenclature).

The odor of the decomposition products of benzenesulfonyl hydrazide is strongly indicative of the presence of thiophenol. This evidence points to an alternate mechanism describing the probable fate of the hypothetical benzenesulfenic acid. The following reactions may be involved (*9*)

$$2\,[R\mathrm{SOH}] \longrightarrow R\mathrm{SH} + R\mathrm{SO_2H} \qquad (2)$$

$$[R\mathrm{SOH}] + R\mathrm{SO_2H} \longrightarrow R\mathrm{SO_2S}R + \mathrm{H_2O} \qquad (3)$$

$$[R\mathrm{SOH}] + R\mathrm{SH} \longrightarrow R\mathrm{SS}R + \mathrm{H_2O} \qquad (4)$$

$$2\,[R\mathrm{SH}] + (\mathrm{O_2})\,(\mathrm{air}) \longrightarrow R\mathrm{SS}R + \mathrm{H_2O} \qquad (5)$$

With these equations in mind it became apparent that a sulfonyl hydrazide would be useful as a commercial blowing agent if it could be modified to produce a nonodorous mercaptan or disulfide residue. Accordingly, a number of variously substituted sulfonyl hydrazides were synthesized and evaluated. Most of them gave adequate blow but few were odorless.

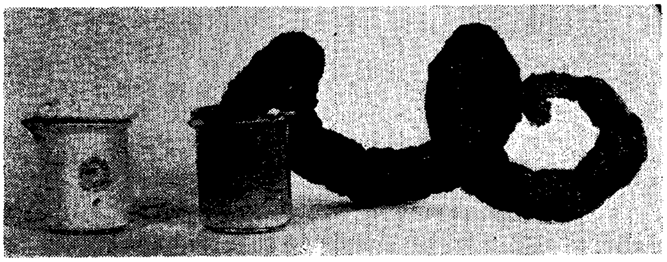


Figure 1. Samples of p,p'-Oxybis-(Benzenesulfonyl Hydrazide)

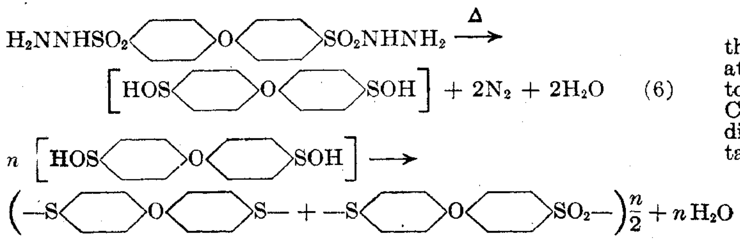
Left. **Before ignition**
Right. **After ignition**

The better approach appeared to be the synthesis of a difunctional sulfonyl hydrazide in the expectation that the decomposition product would be polymeric and, as a result, odorless. A series of such compounds, both aromatic and aliphatic, were prepared and, in general, lived up to expectations. The aliphatic bis-(sulfonyl hydrazides) were not completely satisfactory, but several aromatic compounds left residues entirely without odor. The best of these, with respect to performance and economy, was p,p'-oxybis-(benzenesulfonyl hydrazide), and the balance of the discussion will be devoted to this compound.

p,p'-OXYBIS-(BENZENESULFONYL HYDRAZIDE)

p,p'-Oxybis-(benzenesulfonyl hydrazide) may be prepared by the conventional reaction of the sulfonyl chloride with hydrazine. It is a white, crystalline solid melting with decomposition at 164° C. In solution, or in the presence of rubber or plastics, it decomposes at lower temperatures, although the rate is quite slow at temperatures below 120° C. (248° F.). One gram of the compound should produce 126 ml. of nitrogen under standard conditions; measured gas yields have been above 95% of theory.

By analogy with Equations 1A and 1B its decomposition can be postulated



(6)

(7)

The fact that the decomposition residue is polymeric in nature is easily demonstrated by ignition of the dry blowing agent. Decomposition begins with a smooth gassing off at the point of ignition and spreads slowly throughout the mass. No flame is observed and there results an interesting formation of an insoluble, expanded polymeric foam, reminiscent in form and action of the well-known "Pharaoh's Serpents." Figure 1 is a photograph showing this formation. The insolubility, indicating a 3-dimensional structure, is not in strict keeping with the equations and indicates that unknown side reactions also take place to a limited extent.

Like most hydrazine derivatives, p,p'-oxybis-(benzenesulfonyl hydrazide) decomposes exothermally. The heat of decomposition of the hydrazine portion is partially compensated for by the energy consumed in the reduction of the sulfonyl group. The over-all heating effect during blow is thus quite moderate. This is important in expanded polyvinyl chloride since excessive heat build-up causes discoloration and even charring in the center of thick molded articles. Experimental results show that the hydrazide is superior in this respect to Porofor N, but even so, careful heat control is required in stocks containing high concentrations of the blowing agent.

The true heat of decomposition of p,p'-oxybis-(benzenesulfonyl hydrazide) has not been measured, but some estimations of temperature effects have been made. Five milliliters of a 10% solution of the blowing agent in triethylene glycol was heated rapidly in a vapor bath at 160° C. (320° F.). The solution reached bath temperature in 2 minutes and then increased 4° C. over the next 6 minutes, when the temperature began to drop. Similar temperatures can be expected in small molds. In larger molds or with higher concentrations, the temperature build-up will be greater, and lower press temperatures should be employed.

Figure 2 shows nitrogen evolution data obtained at three temperatures using 1% solutions of the blowing agent in triethylene glycol. The glycol was heated to temperature in a vapor bath and the solid blowing agent was added. The gas evolved was measured in a Hemple gas buret. Fair reproducibility was obtained in spite of the rapid evolution at the higher temperatures. At 131° C. the rate was more moderate, but the polymer began precipitating from solution before decomposition was complete. The decomposition appears to be essentially a first-order reaction and, in this respect, p,p'-oxybis-(benzenesulfonyl hydrazide) resembles Porofor N (*10*).

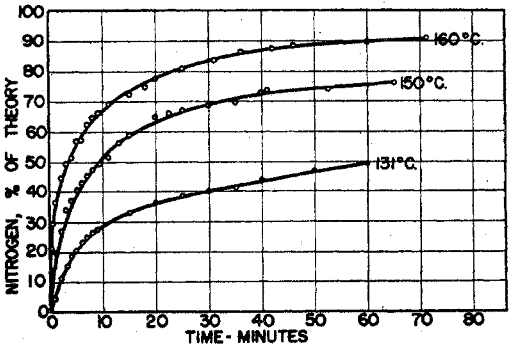


Figure 2. Decomposition of p,p'-Oxybis-(Benzenesulfonyl Hydrazide) in Triethylene Glycol

Examination of the curves shows that evolution of half of the theoretical nitrogen required 3 to 4 minutes at 160° C., 10 minutes at 150° C., and an hour at 131° C. The addition of salicylic acid to the solution had no effect on the rate of decomposition at 131° C., nor did the use of other solvents, including phenol, diphenyl, diphenyl ether, and tricresyl phosphate, have any effect on the total volume of gas evolved at 160° C.

APPLICATIONS

As a blowing agent, p,p'-oxybis-(benzenesulfonyl hydrazide) gives excellent results in both rubber and plastics. It is nontoxic, odorless, nonstaining, nondiscoloring, and produces fine, uniform cell structure. No additional material or catalyst is required for maximum gas evolution. Its high decomposition point permits addition to relatively hot stocks on the mill without danger of premature blow, and compounded stocks can be stored for extended periods prior to cure without loss of blowing efficiency. The hydrazide is a neutral material and has little effect on the cure of rubber or on the stability of polyvinyl chloride.

The practical application of p,p'-oxybis-(benzenesulfonyl hydrazide) as a blowing agent in rubber offers little difficulty. A light-colored, expanded rubber exhibiting fine, uniform cell structure can be made with the following composition:

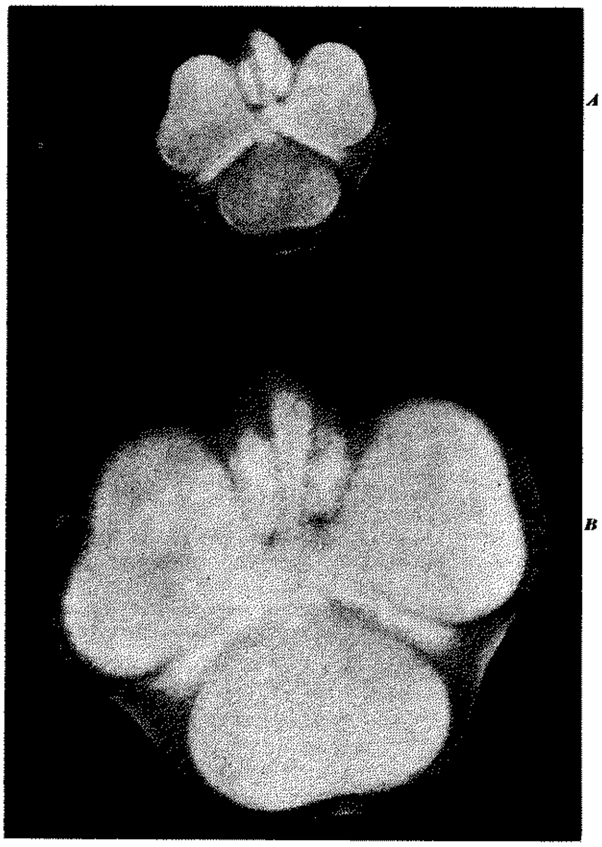


Figure 3. Molded Polyvinyl Chloride

A. Before blow
B. After blow with p,p'-oxybis-(benzenesulfonyl hydrazide)

Pale crepe	100.0
Benzothiazyl disulfide (MBTS)	1.0
Zinc oxide (Protox 166)	5.0
Whiting (Keystone)	30.0
Lithopone	30.0
Stearic acid	10.0
No. 8 oil	10.0
Sulfur	2.5
p,p'-Oxybis-(benzenesulfonyl hydrazide)	1.5

The pale crepe is first broken down on a cold mill to a Mooney viscosity of 20 to 25. The compounding ingredients are then added in the usual manner. The stock is cured in a partly filled mold for 20 minutes at 60 pounds steam temperature. The resulting cellular product exhibits the typical closed cell structure with much finer and more uniform cells than those obtained with bicarbonate.

The new blowing agent can be used to advantage in continuous cure sheet sponge where a free blow is obtained which results in the rupture of many of the cells. When used as the sole blowing agent it gives a resilient product with fine, uniform cell structure. It can also be used effectively as a supplement to soda. The addition of 0.25 to 0.5 part of p,p'-oxybis-(benzenesulfonyl hydrazide) to a conventional soda stock not only improves cell size and uniformity, but also appears to even out the day to day irregularities experienced with soda blow.

Soft, white, unicellular polyvinyl chloride can be made from the following recipe:

Polyvinyl chloride (Marvinol VR-10)	100
Dioctyl phthalate	35
Tricresyl phosphate	65
Stabelan E (stabilizer)	2
Ferro 100 (stabilizer)	2
p,p'-Oxybis-(benzenesulfonyl hydrazide)	18

The composition is blended on a 3-roll paint mill and converted to a smooth plastisol by several passes through the mill. A slight excess of the plastisol is placed in both halves of a split mold, the edges of which must be machined to shoulder tightly and sealed against loss of gas. The mold is closed, placed in a press, and heated under pressure (10 tons on a 3-inch ram) at around 320° F. for 12 minutes. The mold is then thoroughly cooled before the pressure is released. The resulting piece comes out of the mold in a partially expanded form. The expansion is completed by warming to 212° F. for 30 minutes whereby the plastic is softened sufficiently to allow the trapped gas to expand the piece to give the cellular product. The cells formed are barely visible to the naked eye. Figure 3 is a photograph showing a molded article before and after expansion. The volume of the blown sample is approximately ten times that of the original and the definition of the mold is duplicated in good detail.

Figure 4 shows typical cell structures obtained with the new blowing agent in rubber and polyvinyl chloride. A rubber sample blown in the conventional manner with sodium bicarbonate and stearic acid is shown for comparison. The cells of the vinyl foam are so fine as to be almost invisible in spite of the fact that the expansion is nearly four times as great as that of the rubber samples.

Rigid polyvinyl chloride foam can be made from the following formulation:

Marvinol VR-10	100
Diphenyl phthalate	60
Stabelan E (stabilizer)	2
Ferro 100 (stabilizer)	2
p,p'-Oxybis-(benzenesulfonyl hydrazide)	20

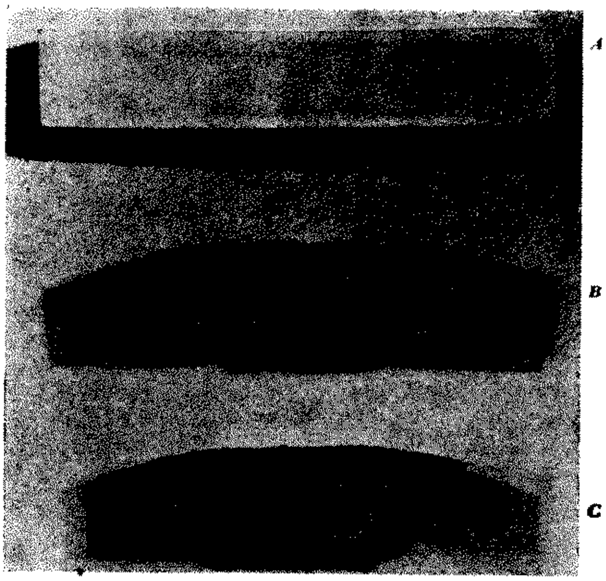


Figure 4. Typical Cell Structures

A. Polyvinyl chloride blown with p, p'-oxybis-(benzenesulfonyl hydrazide)
B. Rubber blown with p,p'-oxybis-(benzenesulfonyl hydrazide)
C. Rubber blown with sodium bicarbonate

The ingredients are premixed and then fluxed on a mill at 260° to 290° F. until good dispersion is obtained and a well-knit sheet is formed. The stock is stripped off the hot mill, allowed to cool and is cut to the desired mold shape. The filled mold is closed and heated under pressure at 320° F. for 4 to 5 minutes. The mold is then thoroughly cooled in the press and the partially expanded piece is removed. The expansion is completed by heating in an oven or in water at 212° F. An alternate method of producing an expanded product is simply to heat the hot-blended compound in an open mold at about 320° F.

Compounds of still lower density can be made by increasing the concentration of the blowing agent. Careful temperature control is required to prevent excessive heat build-up and decomposition of the polyvinyl chloride. This can be accomplished by starting the blow at lower temperatures, followed by an increase in heat if necessary. Heating cycles are also important. When the product is held at elevated temperatures for extended periods, either in the mold or during the final expansion, the gas bubbles coalesce and form larger cells. Thus, each recipe will require some experimentation to achieve the optimal balance of cell structure, final volume, and rate of blow.

A number of other polymers have also been blown satisfactorily using *p,p'*-oxybis-(benzenesulfonyl hydrazide). Included are Butyl rubber, neoprene, GR-S, high reclaim stocks, and various rubber-resin blends. Each of the polymers required a particular set of curing or processing conditions for optimum blow. These conditions, however, appeared to be characteristic of the polymer and were not influenced appreciably by the presence of the blowing agent. Thus it appears that *p,p'*-oxybis-(benzenesulfonyl hydrazide) can find application in the production of a wide variety of expanded, cellular products.

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By-Products of the Thiophene Synthesis

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THE production of thiophene from *n*-butane and sulfur has been described by Rasmussen, Hansford, Sachanen, Myers, and Ray (*5, 15, 16*). The yield of thiophene is about 40% and an equal percentage of a black mobile liquid by-product is formed, which boils above 170° C. at atmospheric pressure and has been classified as thiophene tar. The general properties of this by-product have been described by the same authors (*6*). The present article deals with the composition of this tar and with the two compounds which comprise the bulk of its lower boiling components.

THIOPHENE TAR REFINING

The composition and physical properties of thiophene tar vary when it is kept in storage. In Table I it is shown that the tar, whether refined immediately (fresh tar) or after six months of storage (aged tar), is singularly devoid of free sulfur and hydrogen sulfide and has a constant amount of benzene-insoluble sludge and high molecular weight components. However, the composition of the lower molecular weight portion, usually less than 45% of the total tar, changes considerably during storage.

The lower molecular weight constituents can be isolated from the tar in several ways.

DESTRUCTIVE DISTILLATION. When an aged tar (6 months in storage) is distilled under a vacuum of 1 to 5 mm. of mercury, a 40 to 45% yield of distillate is obtained over a pot temperature range of 80° to 160° C. Above this temperature extensive and uncontrollable decomposition takes place. Redistillation of the distillate at 2 mm. pressure through a column packed with glass helices resolves it into two major components. One component, comprising 30% of the original tar, boils at 40° to 45° C. and the other, comprising 15%, boils at 120° to 125° C. The former has been identified as 3-thiophenethiol. The latter has been classified tentatively as thiolanedithione on the basis of preliminary data concerning its physical and chemical properties.

SOLVENT EXTRACTION. By the use of acetonitrile in a typical 3-stage extraction, an aged tar can be resolved into two equal parts of considerably different molecular weight.

Fraction	Yield, Weight %	Molecular Weight	Sulfur, Weight %
Extract	52	170	57.6
Raffinate	48	350	55.1
Charge (aged tar)	..	280	56.3

TABLE I. ESTIMATED COMPOSITION OF THIOPHENE TARS

Components	Fresh Tar, % by Weight	Aged Tar, % by Weight
3-Thiophenethiol	20–30	<5
3-Thiophenethiol derivative[a]	<5	20–30
Thiolanedithione	10–20	10–20
Free sulfur and hydrogen sulfide	<1	<1
Benzene-insoluble sludge	5–10	5–10
High molecular weight tars, molecular weight >350, average composition[b] $(C_4H_4S_2)_n$	40–50	40–50

[a] Aged product from which 3-thiophenethiol can be regenerated.
[b] Sulfur calculated for $(C_4H_4S_2)_n$, 55.2%; sulfur found, 55.0%.