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Cyanuric Chloride–Sodium Carbonate as Blowing Agent in Rubber and Plastics

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Synopsis

The rates of gas evolution of cyanuric chloride–sodium carbonate, when heated, in dry state, in liquid paraffin, in tricresyl phosphate, and in dibutyl phthalate have been recorded. The mixture has been used as a blowing agent in rubber and the properties of the resulting sponges studied. It has been observed that the retention properties of cyanuric chloride sponge are better than the Vulcacel BN sponge.

INTRODUCTION

The art of making cellular rubber and plastics by the use of blowing agents is about fifty years old. The early blowing agents were gases such as CO_2, NH_3, CH_4, N_2, etc. Later heat unstable chemicals, which on decomposition liberated gases, were used as blowing agents. These were mostly inorganic chemicals, such as ammonium carbonate, ammonium nitrite, sodium bicarbonate. The difficulty of evenly dispersing these inorganic chemicals in rubbers led to the use of thermally unstable organic chemicals as blowing agents. All these organic blowing agents on decomposition give either one of the following gases: CO_2, N_2, N_2O, NH_3, H_2O, or mixtures of these gases. However most of modern blowing agents, which have found favor in industry, invariably liberate nitrogen on decomposition.

CYANURIC CHLORIDE

Due to its cheap manufacture, cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) has been increasingly used in industry for the last several years. The chlorine atoms in the molecule have high reactivity and are easily hydrolyzed by water vapor to different hydroxy derivatives and hydrochloric acid. It does not decompose when heated up to 190°C.[1] and is soluble in dioxane, acetone, benzene, chloroform, methylene chloride, carbon tetrachloride, etc.

BLOWING AGENT

Dumont and Reinhardt[2] appear to be the first to report Genitron THT—trihydrazide—as a new blowing agent from cyanuric chloride. On de-

composition at 316°C. it gives nitrogen and ammonia as gaseous products.

Cyanuric chloride and sodium carbonate, when heated separately at 150°C., do not liberate gaseous products. However, it has been observed, that when a mixture of these two chemicals is heated in dry state or in liquid medium (paraffin), gaseous products are liberated. It was therefore decided to study this mixture as a blowing agent in rubber and plastics.

Here is an instance of an intimate mixture of an organic chemical and an inorganic chemical, being used as a blowing agent. Cyanuric chloride probably reacts quickly, within the liquid medium (paraffin) generating hydrochloric acid, which when coming in contact with sodium carbonate liberates carbon dioxide and water as gases:

$$2HCl + Na_2CO_3 \rightarrow NaCl + CO_2 + H_2O$$

Thus, theoretically one mole of cyanuric chloride will liberate three moles of gaseous products i.e., 364 cc. gas/g. cyanuric chloride. Table I

TABLE I

Gas Volume Evolved by Blowing Agents

Blowing agent	Temp. °C.	Gas volume, cc./g. blowing agent
X-950	120	374
Nitrourea	129	380
Genitron AC	209	438
Genitron THT	316	247
Cyanuric chloride + sodium carbonate	118	309

gives the quantity of gas liberated by some of the modern blowing agents[3] at the temperature of their decomposition.

Figure 1 shows the rate of gas evolution, in a standard apparatus, of a cyanuric chloride–sodium carbonate (anhydrous) mixture, in the dry state and in liquid paraffin. In the dry state (curve *A*) the gas released at 115°C. is very irregular and is about 29% of the theoretical. In liquid paraffin (curve *B*), in 20 min., about 85% of the gas has been released at a controlled rate.

Since the present blowing agent is an intimate mixture of an organic chemical and an inorganic chemical, representative curves of gas evolution in liquid paraffin, of blowing agents belonging to the two classes have been reproduced in Figure 2. In the case of X-950, an organic blowing agent, the rate of gas evolution is very rapid and in less than 10 min. about 100% of the gas is evolved. In the case of sodium bicarbonate, an inorganic blowing agent which has been used in rubber mixes for a number of years the rate of gas evolution is very erratic and continues over a longer period of time.[4]

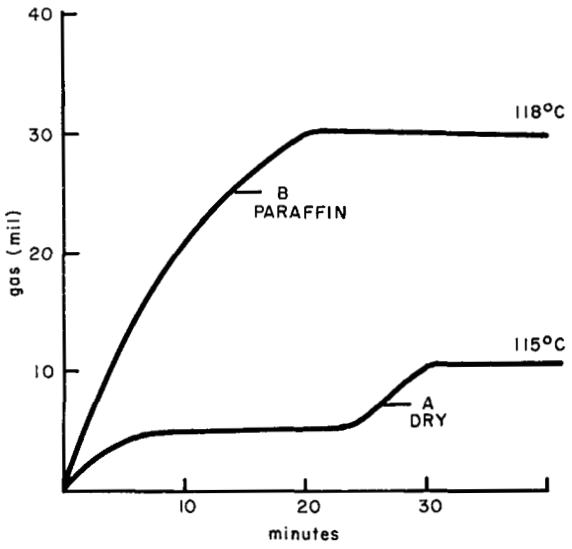

Figure 1.

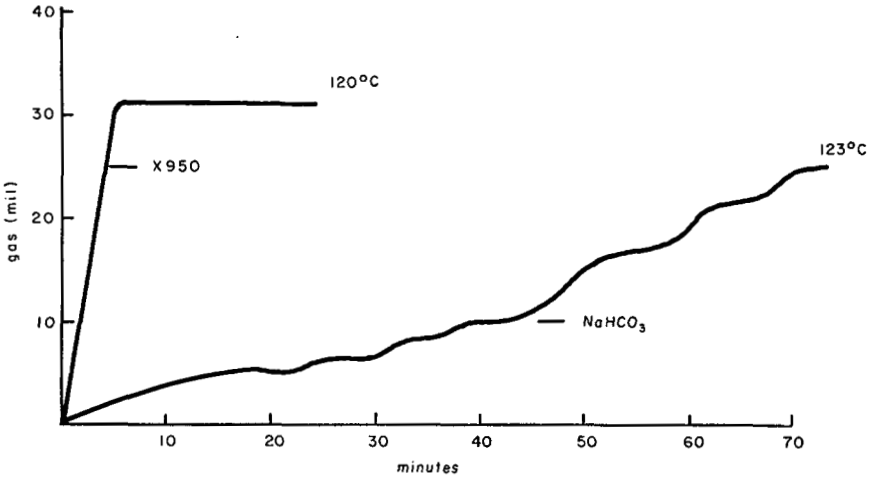

Figure 2.

RUBBER SPONGE

The cyanuric chloride–sodium carbonate mixture, which has a maximum gas evolution temperature at 118°C., is used to make rubber sponges. The effect of this blowing agent on the cure time and on the aging properties of a standard rubber mix (Table II), in comparison to a standard blowing agent Vulkacel BN, is shown in Table III.

DISCUSSION

The tensile strength of cyanuric chloride sponge is lower than that of the Vulcacel BN sponge. This probably is due to uneven pour size of the cyanuric chloride sponge, resulting from the difficulties in dispersion of

TABLE II

Sponge Rubber Formulations[a]

	Wt., g.	Wt., g.
Rubber	100.00	100.00
Vulcamel TBN	0.60	0.60
Nonox D	1.00	1.00
Zinc oxide	5.00	5.00
Stearic acid	5.00	5.00
China clay	67.00	67.00
Petroleum jelly	8.00	8.00
MBT	0.75	0.75
ZDC	0.25	0.25
Sulfur	2.50	2.50
Cyanuric chloride–sodium carbonate	1.00	—
Vulcacel BN	—	1.00

[a] Both the mixes were made according to the A.S.T.M. method; cure: 10 min. at 149°C.

cyanuric chloride–sodium carbonate in the rubber mix. Cyanuric chloride, being lachromatic, presents difficulties during milling on an open rubber mill.

TABLE III

Physical Properties of the Sponges

	Cyanuric chloride–sodium carbonate			Vulcacel BN		
Property	Initial	7 days at 70°C.	14 days at 70°C.	Initial	7 days at 70°C.	14 days at 70°C.
Hardness (Shore A)	20			20		
Tensile strength, psi	1190	1120	1100	1600	1300	1285
Modulus at 300%, psi	360	530	550	500	650	550
Elongation at break, %	500	475	550	600	500	615

The effects of aging in a Scott's block at 70°C. for 14 days on the tensile strengths and 300% moduli of the sponges are shown in Figures 3 and 4. The fall in tensile strength due to aging of the cyanuric chloride sponge is much less than the corresponding fall in tensile strength of the Vulcacel BN sponge. The 300% moduli in both the sponges increase up to 7 days

aging. After 14 days of aging there is a fall in modulus of the Vulcacel BN sponge and a slight rise in the modulus of the cyanuric chloride sponge.

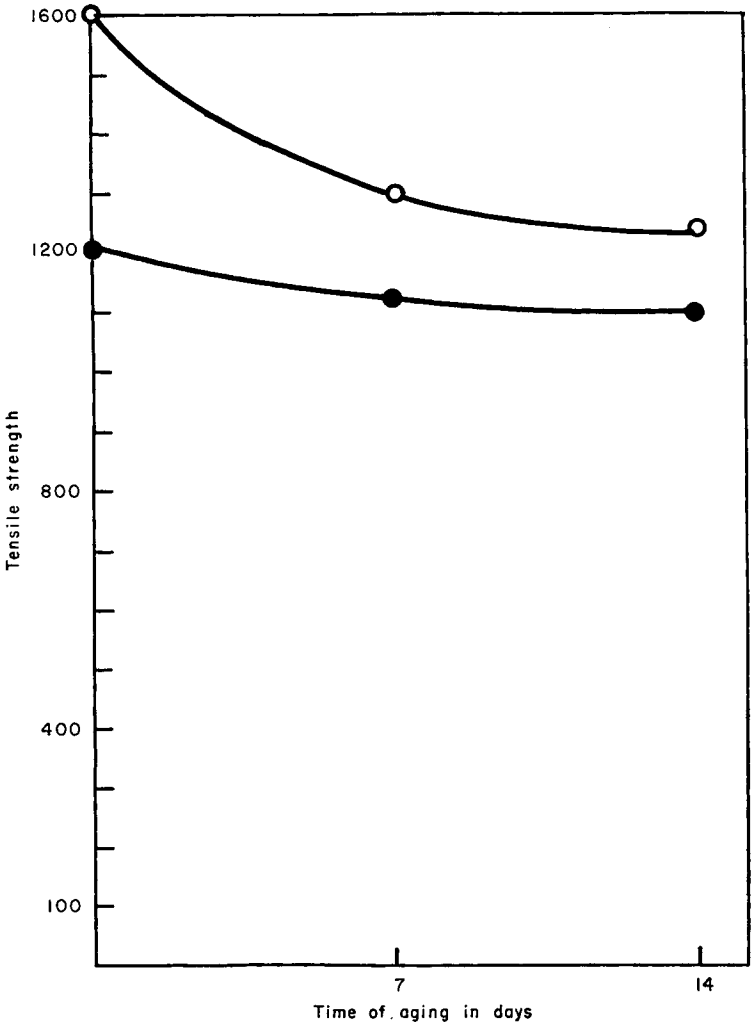

Figure 3.

Thus it is observed that the cyanuric chloride sponge has better retentive properties than the Vulcacel BN sponge.

PVC Sponge

To determine whether this blowing agent is suitable for making PVC sponges, it was decided to see the effect of common PVC plasticizers such as tricresyl phosphate and dibutyl phthalate on the rate of gas evolution in these media. Figure 5 shows that in tricresyl phosphate, the gas evolved at

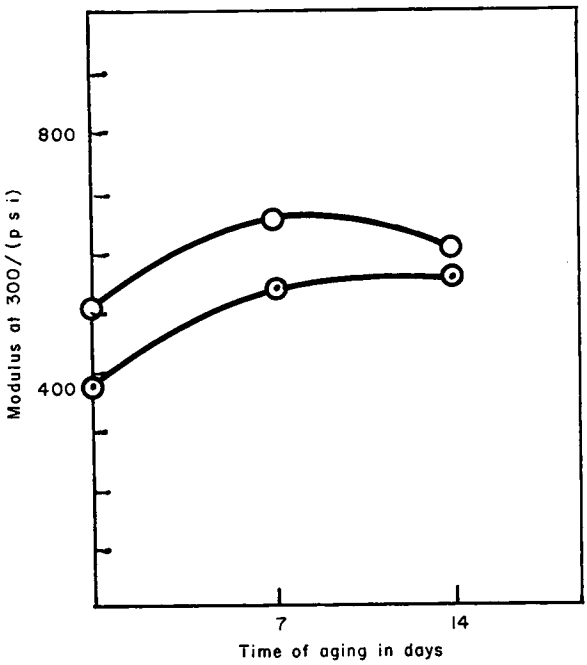

Figure 4.

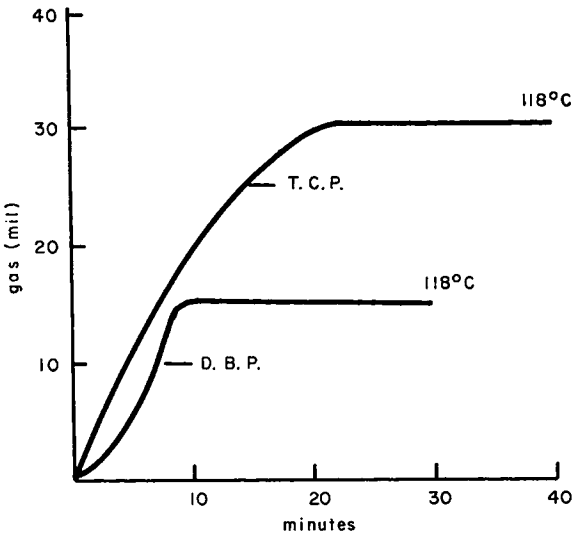

Figure 5.

118°C. is 85% of the theoretical, whereas in dibutyl phthalate the gas evolved is only 42%. Thus this blowing agent can best be used to make cellular PVC when tricresyl phosphate is the plasticizer.

Advantages and Disadvantages of the Blowing Agent

Advantages of the cyanuric chloride–sodium carbonate blowing agent are: (*a*) the gas is released over a definite and shorter range of temperature; (*b*) the gas is released at a controlled and a rapid rate; (*c*) the gas released is noncorrosive; (*d*) the blowing agent is colorless, and the residual products of decomposition does not stain the resultant cellular sponge; (*e*) the blowing agent is not inflammable; (*f*) there is no large exotherm on heating at 118°C.; (*g*) the cure rates of the standard rubber mixes are not affected by the use of this blowing agent.

Disadvantages of this mixture are (*a*) the blowing agent is lachromatic; (*b*) the efficiency of the blowing agent is affected in a moist environment; (*c*) the blowing agent is not easily dispersed in rubber mixes, due to the presence of inorganic chemical.

CONCLUSIONS

The present blowing agent can be used for making rubber and PVC sponges. However the presence of sodium carbonate and the lachromatic nature of cynanuric chloride make the dispersion of this blowing agent in rubber mixes extremely difficult on an open rubber mill. The dispersion may be achieved with some ease by reducing the particle size of sodium carbonate by ball milling. Processing of the rubber mix with this blowing agent in a closed rubber mill (Banbury type) will help the processor to avoid the lachromatic effects of cyanuric chloride.

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Résumé

On a enrégistré les vitesses de dégagement gazeux du mélange chlorure cyanurique carbonate de sodium, lorsqu' on les chauffe à l' état sec dans la parafine liquide, de phosphate tricrésyle et le phtalate de dibutyle. Le mélange a été employé comme agent

moussant et on a étudié les propriétés des éponges qui en résultent, On a observé que les propriétés de rétention des éponges formées à partir de chlorure cyanurique sont meilleures que celles des éponges obtenues à partir de Vulcacel BN.

Zusammenfassung

Die Geschwindigkeit der Gasentwicklung beim Erhitzen von Cyanurchlorid–Natriumcarbonat-Gemischen in trockenem Zustand sowie in flüssigem Paraffin, Trikresylphosphat und Dibutylphthalat wurde bestimmt. Die Mischung wurde als Treibmittel in Kautschuk verwendet und die entstehenden Schwämme untersucht. Die Cyanurchlorid-Schwämme haben bessere Retentionseigenschaften als Vulcalcel-BN-Schwämme.

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