Low-melting sulphate glasses and glass–ceramics, and their utility as fire and smoke retarder additives for poly(vinyl chloride)

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Low-melting sulphate glasses and glass–ceramics, which are effective fire and smoke retarder additives for poly(vinyl chloride) (PVC), have been developed. They are based on low-melting, glass-forming compositions in the K_2SO_4–Na_2SO_4–$ZnSO_4$ ternary system. The preferred ternary sulphate glass melts at 420° C and has the composition $K_2SO_4 \cdot Na_2SO_4 \cdot 2ZnSO_4$, which also corresponds to the composition of a congruently melting ternary compound. In a simple, tin-stabilized PVC compound, 10 phr (parts per hundred of resin) resulted in a 54% reduction in smoke in the flaming mode of the NBS Smoke Chamber. 40 phr gave a smoke reduction of 83%. The preferred ternary sulphate glass also works in concert with low levels of other known smoke retarders. For example, 10 phr of the ternary glass and 5 phr of MoO_3 gave a smoke reduction of 78%, while 40 phr of the glass and 5 phr of MoO_3 gave a smoke reduction of 93%. The addition of transition metal sulphates to low-melting compositions in the K_2SO_4–Na_2SO_4–$ZnSO_4$ system led to the development of low-melting glasses and glass–ceramics containing Ni^{2+}, Cu^{2+} and VO^{2+}. These transition metal modified sulphates were also very effective smoke retarders in the simple PVC compound. All of the low-melting sulphate glasses and glass–ceramics promoted intumescence and char formation during combustion of the simple PVC compound. In this way they effectively formed thermal barriers to retard further combustion.

1. Introduction

Low-melting vitreous phases are potentially useful polymer additives. Low melting is arbitrarily defined here to designate glasses which can soften and flow under the influence of either gravity or gases functioning as blowing agents, at temperatures less than ~ 500° C. The theme of this paper is the development of low-melting glasses which soften and flow at temperatures which promote thermal degradation and combustion of polymer compounds containing them.

In principle, low-melting glasses can improve the thermal stability and flammability characteristics of polymer compounds by

1. Providing a thermal barrier for both undecomposed polymer and the char, if any, which forms as a combustion product.

2. Providing an oxidation barrier to retard oxidation of the thermally degrading polymer and its combustion char residue.

3. Providing a "glue" to hold the combustion char together and give it structural integrity.

4. Providing a coating to cover over or fill in voids in the char, thus providing a more continuous external surface with a lower surface area.

Finally, low-melting glasses can be potentially useful components of intumescent polymer additive systems. They would provide a fluid, viscous phase to be expanded and blown by escaping gases. The formation of a vitreous or non-vitreous inorganic insulating foam is not an unreasonable expectation.

The polymer chosen for this study is poly(vinyl chloride) (PVC). It is a naturally fire-retardant polymer which has a Limiting Oxygen Index of about 43. However, when it is forced to burn, it generates large quantities of smoke. Recently, it has been shown that a large number of metal compounds, when used as smoke and fire retarder additives in rigid PVC compounds, act to significantly retard the generation of smoke and to enhance the conversion of the PVC into a thermally stable char [1–3]. The mechanistic role of these smoke retarders has been studied in some detail for selected compounds of molybdenum and copper [2, 3, 4–8]. For the purpose of this discussion, it is sufficient to recognize that they change the normal thermal degradation pattern of PVC which generates a significant amount of volatile aromatic hydrocarbons, which can be equated with smoke and constitutes a significant fuel source which acts to support combustion. The generation of combustible aromatic hydrocarbons is replaced by the formation of a thermally stable char. This effectively reduces the fuel content available to support combustion and eliminates the major contributor to smoke.

The objective of this research was to develop low-melting glass systems as smoke and fire retarder additives for rigid PVC. The approach was to develop

glasses containing metals which were known to form effective smoke and fire retarder additive compounds for PVC. Such glasses, of course, would have to be readily friable so that they can be readily incorporated into PVC as a fine pigment. Furthermore, candidate glasses should soften or melt at temperatures around 500° C and be able to coat the decomposing polymer and its combustion char, and act as a thermal barrier to combustion and oxidation of the char and the polymer.

The low-melting glasses described in this paper are based on zinc sulphate, $ZnSO_4$. This choice was made for a number of reasons. One of them was the known fact that low-melting glasses could be made from various compositions in the K_2SO_4–$ZnSO_4$ binary system [9]. Another was that zinc compounds in general, and $ZnSO_4 \cdot xH_2O$ specifically, have been shown to be effective smoke and fire retarder additives for PVC [1].

Preliminary experiments verified that glasses could be formed from certain compositions of the K_2SO_4–$ZnSO_4$ binary system. However, these glasses were difficult to form because they readily devitrified, even with relatively fast quenching to room temperature. In addition, there is only a very limited low-melting region in the K_2SO_4–$ZnSO_4$ system. Frequently, the addition of an appropriate third component to a binary system will give rise to ternary composition regions with lower liquidus temperatures. I therefore investigated the possibility of forming stable, low-melting glasses from the Na_2SO_4–K_2SO_4–$ZnSO_4$ ternary system.

2. Experimental procedure
2.1. Composition and preparation of the sulphate glasses
The raw materials used in preparing the sulphate glasses and the modified sulphate glass compositions are identified in Table I.

The usual method of preparing the sulphate glasses is described below:

1. A mixture of the hydrated or anhydrous component sulphates is ground together in a mortar and pestle.

2. The ground mixture is contained in a porcelain dish and placed in an electric muffle furnace maintained at 560° C.

3. After 1 h, the clear melt is removed from the furnace and cast into a transparent plate by pouring it on to a cold iron or aluminium plate. In order to minimize or eliminate devitrification of the glass, the quench plate is cooled to dry-ice temperature.

4. The glass plate is broken into small chunks and ground into a fine powder using a Siebtechnik grinder.

2.2. Preparation of the experimental PVC compounds
The sulphate glasses or crystalline sulphates were evaluated as fire and smoke retarders in a simple PVC compound which is described below:

100 parts Geon 103EP PVC resin
  2 parts Microthene 510 polyethylene processing aid

TABLE I Materials used in preparing sulphate glasses

Name	Formula	Source
Zinc sulphate crystal	$ZnSO_4 \cdot 7H_2O$	Fisher Z–68
Zinc sulphate monohydrate	$ZnSO_4 \cdot H_2O$	Fisher Z–68*
Potassium sulphate powder	K_2SO_4	Fisher P–305
Sodium sulphate	Na_2SO_4	Fisher S–421
Aluminium sulphate	$Al_2(SO_4)_3 \cdot 18H_2O$	Fisher A–613
Cerium(IV) sulphate	$Ce(SO_4)_2$	Fisher C–258
Cadmium sulphate	$CdSO_4$	Fisher C–20
Manganese(II) sulphate	$MnSO_4 \cdot H_2O$	Fisher M–113
Nickel(II) sulphate	$NiSO_4$	K & K† 28171
Copper(II) sulphate	$CuSO_4$	Baker 1850
Vanadyl sulphate	$VOSO_4 \cdot 2H_2O$	Fisher V–8

*Prepared from $ZnSO_4 \cdot 7H_2O$ by heating it in air at $\sim 135°$ C overnight.
†Refers to K & K Laboratories

  2 parts dibutyltinthioglycolate stabilizer

The PVC compounds containing the sulphate additives were prepared using conventional laboratory polymer processing procedures. First, the PVC resin and polyethylene processing aid were banded on a hot ($\sim 160°$ C) rolling rubber mill. After addition of the tin stabilizer, the sulphate additives, and any additional smoke retarder, the milling was continued for about 5 min. Finally, the milled compound in sheet form was hot-pressed at $\sim 166°$ C into the test specimen configurations defined under the individual combustibility tests.

2.3. Combustibility test procedures
The flammability characteristics of the PVC compounds containing the sulphate glasses and related crystalline sulphates were determined using three small-scale laboratory combustion tests. The performance of the PVC compounds in these tests does not necessarily correspond to their performance in either large-scale tests or large-scale real fires.

The NBS Smoke Chamber Test was run in accordance with ASTM E–662–79, "Test for Specific Optical Density of Smoke Generated by Solid Materials". All tests were conducted under flaming conditions where PVC generates the most smoke. In this test, 7.3 cm $\times$ 7.3 cm $\times$ 0.06 cm samples are exposed to a radiant heat source of 2.5 W cm^{-2} until the exposed part of the sample has stopped emitting smoke. A small pilot flame is located immediately in front of the sample in order to ignite flammable decomposition gases. The smoke evolved is measured photometrically by monitoring the optical density of the smoke which accumulates in the closed smoke chamber. The NBS Smoke Number reported in this paper, D_m/g, is the optical density smoke number normalized to the weight in grams of the test specimen.

The Goodrich Smoke-Char Test is a small-scale laboratory test which was designed to measure both the formation of smoke and char. It has been described in detail in an earlier publication [1]. A small, ~ 0.3 g, solid sample, ~ 0.19 cm thick, is exposed to a reproducible and well-regulated (276 Pa) propane flame from a Bernzomatic type burner for a period of 1 min. The generated smoke rises through a glass chimney and passes through the beam of a

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photocell coupled to an integrating circuit. The integrated area, when normalized to the weight of PVC in the sample, gives the Smoke-Char Smoke Number, S_{PVC}. As soon as the 1 min burn time has been reached, the flame is extinguished and the sample residue, char, is quenched in a rapid stream of nitrogen. The char yield is calculated from the weight loss observed during burning. It is expressed as %BC, the percentage of the PVC backbone (that part of the hydrocarbon backbone left after complete dehydrochlorination) retained as a char residue. It is calculated as

$$\%BC = \frac{Char\ wt\ -\ Nonburnable\ residue\ wt}{Sample\ wt\ -\ Non\text{-}PVC\ wt\ -\ HCl\ wt} \times 100$$

The Torch Test has been developed by Dickens of our laboratory to study char formation and intumescence behaviour during combustion [10]. It provides a visual observation of the char formation which occurs when a vertically mounted sample is exposed to a horizontally mounted propane torch operating under a specified set of reproducible conditions. The thermal protection afforded by the char is measured as the time necessary for the back-side temperature of the sample to reach 250° C. The following conditions were used:

1. Sample size: pressed plate 3.65 cm square and 0.19 cm thick.

2. Initial temperature: room temperature to $\leq 50°\ C$.

As will be discussed later in this report, the Torch Test is a very qualitive test, the reproducibility of which is highly dependent on the mode of failure of the barrier char.

3. Results and discussion
3.1. Ternary base glass selection
Glass-forming compositions were sought in the Na_2SO_4–K_2SO_4–$ZnSO_4$ ternary system. This system was chosen because it contains a large region of relatively low ($< 500°\ C$) liquidus temperatures, and because sulphate glasses have been reported for certain K_2SO_4–$ZnSO_4$ binary compositions [9]. The phase diagram of the Na_2SO_4–K_2SO_4–$ZnSO_4$ ternary system in the $ZnSO_4$-rich, low-melting region is shown in Fig. 1 [11].

An attempt was made to prepare two glasses from the K_2SO_4–$ZnSO_4$ binary system and two glasses from the K_2SO_4–Na_2SO_4–$ZnSO_4$ ternary system. The results of these initial synthesis attempts are summarized in Table II. In contrast to the results reported in Table II, when melts of Composition I and 3 are

quenched at room temperature, they form partly crystallized glasses. In the cases where homogeneous melts were obtained, the melts had a low viscosity as soon as the melt temperature was about 20° C above the liquidus temperature. For example, the ternary Glass 3 could only be drawn into fibres within a very narrow temperature range which occured just before the glass solidified. Glass 3 was selected to be the representative base sulphate glass for evaluation in the model PVC compound. It is a better choice than the binary Glass 1 for the following reasons:

1. It corresponds to the composition of the $1:1:2$ K_2SO_4–Na_2SO_4–$ZnSO_4$ ternary compound shown in Fig. 1. Therefore, if it partly crystallizes, the crystalline compound will be the complex $1:1:2$ sulphate. In addition, if the glass composition deviates slightly from the ideal $1:1:2$ composition, it will still remain within the primary crystalline phase field of the $1:1:2$ ternary compound. That is, if the glass begins to crystallize, the first crystalline compound to form will be the $1:1:2$ compound. Conversely, if a mixture of the ternary Glass 3 and the $1:1:2$ sulphate is heated to above 420° C, a homogeneous melt with the $1:1:2$ stoichiometry will result immediately.

2. Glass 1 lies within the primary crystalline phase field of a relatively simple $1:2$ K_2SO_4–$ZnSO_4$ binary compound. This is an important distinction compared to the crystallization behaviour of the ternary Glass 3. The Zn^{2+} ions in the $1:2$ binary compound may be more reactive and more likely to cause an undesirable degradation of PVC during processing, compared to the $1:1:2$ ternary compound. This is a real concern because of the well-known effect of zinc ions on promoting the thermal degradation of PVC.

3. Glass 3 melts at a lower temperature than Glass 1.

4. Glass 3 contains less Zn^{2+} which can cause processing problems in PVC.

3.2. NBS Smoke Chamber evaluation of $ZnSO_4$-based glasses
Glasses 1 and 3 were added to the model PVC compound at both the additive level (10 phr) and the filler level (40 phr). At both levels, PVC compounds containing the glasses and an additional condensed-phase smoke retarder system were prepared and tested. The condensed-phase smoke retarder systems were molybdenum trioxide, MoO_3, and a $1:4$ weight ratio of alpha-iron oxide, Fe_2O_3, and nickel(II) oxide, NiO.

The NBS Smoke Chamber evaluation of the sulphate glass containing PVC compounds is summarized in Tables III and IV. PVC compounds containing 10 and 40 phr of $BaSO_4$ are also included in the results in Table III. This is because $BaSO_4$ substan-

TABLE II Preparation of zinc sulphate binary and ternary glasses

Identification	Composition (mol %)			Liquidus Temperature (°C)	Melting Temperature (°C)	Melt	Glass*
	K_2SO_4	Na_2SO_4	$ZnSO_4$				
1	40	–	60	~450	560	Clear	Clear
2	57	–	43	450	575	Inhomogeneous	Partly Devitrified
3	25	25	50	420	560	Clear	Clear
4	33	26.4	40.6	384	530	Clear	Partly Devitrified

*These results are for melts which were quenched by pouring them on to a massive polished aluminium plate cooled to dry-ice temperature.
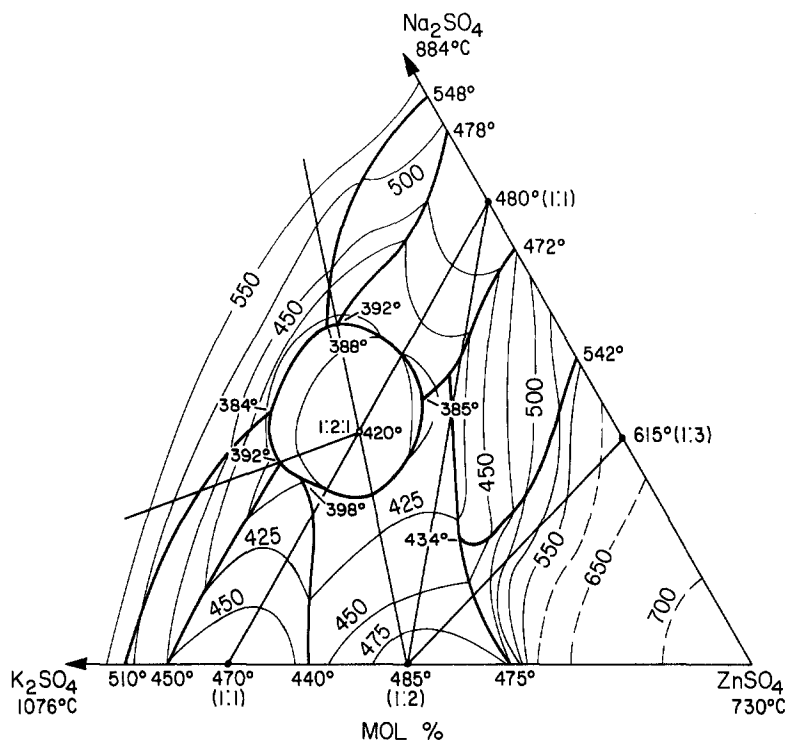
Figure 1 Low-melting, high zinc sulphate region of the Na_2SO_4–K_2SO_4–$ZnSO_4$ ternary system from [10]. The glass-forming region of ternary compositions practically lies within the region bordered by the 450° C isotherm.

tially acts as a chemically inert diluent in PVC. Therefore, the $BaSO_4$-containing compounds provide secondary controls which make it easier to recognize smoke retarder activity originating from the sulphate glasses.

The conclusions to be drawn from Tables III and IV are obvious. The zinc sulphate-based glasses are effective smoke retarders for PVC at both additive and filler levels. Furthermore, they interact in a complementary fashion with established condensed-phase smoke retarders. The result is the potential ability to design very low-smoke model PVC compounds based on zinc sulphate glasses.

The utility of sulphate Glass 3 as a smoke retarder additive in the model PVC compound is illustrated in Fig. 2. It is a plot of the NBS Smoke Number (D_m/g), against the level of $BaSO_4$, Glass 3 and MoO3 added to the control PVC compound. Compared to $BaSO_4$, Glass 3 and the Glass 3 mixtures with the 5 phr MoO_3

system gave large reductions in smoke which cannot be explained in terms of simple dilution effects.

Between 10 and 40 phr, the curves for Glass 3 and the "inert" $BaSO_4$ have similar shape and smoke characteristics. This suggests that increasing the level of ternary Glass 3 from 10 to 40 phr makes the PVC compound more smoke-retardant by the process of dilution. The same argument could be made in terms of the Glass 3 combination with 5 phr MoO_3. In contrast, the differences between the three curves at any total additive concentration illustrate the potential of both ternary Glass 3 and its combination with 5 phr MoO_3 to be condensed-phase smoke retarders in the model PVC compound.

3.3. Torch Test evaluation of the ternary Glass 3

The Torch Test provides a qualitative observation of the intumescence effect, if any, provided by the

TABLE III NBS Smoke Chamber evaluation of PVC containing low levels of low-melting sulphate glasses

Additives (phr)					$D_m/g^†$	Smoke decrease[‡] (%)
Ternary Glass 2	Ternary Glass 3	$BaSO_4$	MoO_3	Fe/Ni[*]		
—	—	—	—	—	77 ± 2	—
—	—	10	—	—	65 ± 1	16
—	—	—	5	—	27 ± 2	65
—	—	10	5	—	25 ± 1	68
—	—	—	—	5	17 ± 0	78
—	—	10	—	5	16 ± 0	79
10	—	—	—	—	32 ± 6	58
10	—	—	5	—	20 ± 3	74
10	—	—	—	5	16 ± 1	79
—	10	—	—	—	35 ± 2	54
—	10	—	5	—	17 ± 1	78
—	10	—	—	5	13 ± 1	83

[*] 1 : 4 weight ratio of Fe_2O_3/NiO.
[†] NBS Smoke Chamber Smoke Number per gram of sample tested.
[‡] Percentage decrease in smoke relative to the control (no additives).

TABLE IV NBS Smoke Chamber evaluation of PVC containing high levels of low-melting sulphate glasses

Additives (phr)				D_m/g*	Smoke decrease[†] (%)
Ternary Glass 2	Ternary Glass 3	BaSO$_4$	MoO$_3$		
—	—	—	—	82 ± 1	—
—	—	40	—	46 ± 1	44
—	—	—	5	28 ± 3	66
—	—	40	5	21 ± 3	74
40	—	—	—	23 ± 2	72
40	—	—	5	10 ± 1	88
—	40	—	—	14 ± 1	83
—	40	—	5	6 ± 0	93

*NBS Smoke Chamber smoke number per gram of sample tested.
[†]Percentage decrease in smoke relative to the control (no additives).

addition of smoke and fire retarder additives to polymer compounds. It also provides information about the thermal stability of the char which forms during burning and how well the char serves as a protective thermal barrier for the underlying material. The time to failure is defined as the time required for the temperature on the back side (opposite the impinging flame front) to reach 250° C. Failure times of 5 min or longer suggest that the char is acting efficiently as a protective thermal barrier.

The PVC samples described in Tables III and IV were evaluated in the Torch Test. At both the additive and filler levels, the sulphate glasses acted as intumescent agents in the control PVC compound. In the same way, the addition of MoO$_3$ or the Fe$_2$O$_3$-NiO smoke retarder systems to the control compound gave a moderate intumescent effect. However, this effect was enhanced when the sulphate glasses were added along with the metal oxide smoke-retarder systems.

The evaluation of ternary Glass 3 in the Torch Test is summarized in Table V. The data show that the addition of 10 to 40 phr of the ternary Glass 3 gave about a seven-fold increase in thermal protection relative to the PVC control. However, it can be seen that

the very effective MoO$_3$ and Fe$_2$O$_3$-NiO smoke-retarding and char-forming additive systems gave even more effective protection. In the case of MoO$_3$, the level of thermal protection was significantly increased when 10 phr of Glass 3 was added. In contrast, the addition of 10 phr of Glass 3 did not improve the protection afforded by 5 phr of the Fe$_2$O$_3$-NiO system itself, even though there was a greater intumescent effect. The addition of 40 phr of Glass 3 to the model PVC compound did not afford more thermal protection than the addition of only 10 phr of the glass. In fact, in the samples containing 5 phr of MoO$_3$, 10 phr of ternary Glass 3 gave more thermal protection than 40 phr of the glass.

The thermal protection data in Table V should be treated in a qualitative sense only. One reason for this is that the scatter in the experimental results which led to the average protection times reported in Table V was relatively large. Another reason is that it is difficult to determine at what level the differences in protection time we observe in the Torch Test reflect significantly different levels of thermal protection.

The key factor which limits the thermal protection afforded by the low-melting sulphate glasses in PVC appears to be their low melt viscosities. Low-melting sulphate glasses with improved thermal protection characteristics will have to be sought by making significant changes in composition. Such modified sulphate glass compositions and their evaluation as
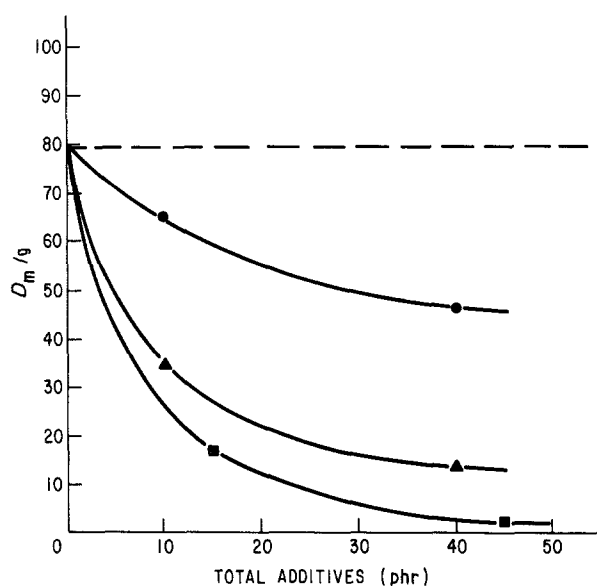

Figure 2 Efficacy of the ternary sulphate Glass 3 to be a smoke retarder additive for PVC. D_m/g is the Smoke Number from the NBS Smoke Chamber Test conducted in the flaming mode. BaSO$_4$ is included to show the effect from adding an "inert" diluent. (———) PVC control, (●) BaSO$_4$, (▲) ternary Glass 3, (■) ternary Glass 3 + 5 phr MoO$_3$.

TABLE V Torch Test evaluation of PVC containing the ternary low-melting sulphate Glass 3

Additives (phr)				Protection Time[†] (sec)
Ternary Glass 3	BaSO$_4$	MoO$_3$	Fe/Ni*	
—	—	—	—	30 ± 1
—	10	—	—	44 ± 0
—	—	5	—	471 ± 63
—	—	—	5	399 ± 91
—	10	5	—	525 ± 290
—	10	—	5	247 ± 5
10	—	—	—	220 ± 43
10	—	5	—	752 ± 166
10	—	—	5	326 ± 82
—	40	—	—	91 ± 6
—	40	5	—	440 ± 202
40	—	—	—	213 ± 66
40	—	5	—	323 ± 32

*1 : 4 weight ratio of Fe$_2$O$_3$/NiO.
[†]Time for the back of the sample to reach 250° C.

smoke and fire retarded additived in PVC are covered in Section 3.6 of this paper.

3.4. Processing characteristics of the ternary base glass

Up to 40 phr of the ternary sulphate Glass 3 is readily incorporated into the model PVC compound using a hot rubber mill. This is accomplished without discoloration of the PVC, even in the presence of the tin stabilizer. The ternary sulphate Glass 3 had been mechanically ground into a fine, white powder before being added to the PVC compound. The index of refraction of the powdered glass is apparently very close to that of the PVC model compound. For example, with the exception of a slight speckled effect from the largest glass particles, the addition of up to 40 phr of the ternary Glass 3 did not significantly pigment the PVC. In fact, hot-pressed PVC plates containing 40 phr of Glass 3 tended to be translucent.

There is one other important potential reason for chosing the ternary Glass 3 instead of its devitrified form, a mixture of its component sulphates of identical stochiometry, or $ZnSO_4 \cdot H_2O$. This reason is the anticipated processing advantage of the sulphate glass relative to the other forms of the same composition. The sulphate glass will have a lower surface area and thus fewer reactive zinc ions than any of its comparable forms, or the closely related $ZnSO_4 \cdot H_2O$.

3.5. Comparison of amorphous and crystalline sulphate compositions

Certainly from the standpoint of forming a melt, the need for a glass or a low-melting homogeneous crystalline composition is necessary for an intumescent application. But what if the main concern is only to use the "glass" as a smoke retarder? In the case of the ternary sulphate Glass 3, for example, one must consider if there is an advantage in using as a smoke retarder

1. The ternary glass.

2. The crystallization product of the ternary glass, which is a congruently melting sulphate compound.

3. A mixture of the component sulphates which is equivalent to the ternary glass.

The effectiveness of the ternary sulphate Glass 3 as a smoke retarder in PVC was compared to its crystallization product, and to a mixture of K_2SO_4, Na_2SO_4 and $ZnSO_4 \cdot H_2O$ of the same stochiometry. The devitrified (crystallized) glass was prepared by heating a sample of the ternary glass in air at 300° C for about 18 h. The X-ray diffraction pattern of the devitrified glass was different from those reported for any of the component sulphates and their binary compounds. Presumably it corresponds to the $1:1:2$ K_2SO_4–Na_2SO_4–$ZnSO_4$ ternary compound of the same composition as ternary Glass 3. The preparation of the $ZnSO_4 \cdot H_2O$ is described in Section 2. The sulphate mixture with the stochiometry of Glass 3 was prepared by grinding together in a Siebtechnik grinder K_2SO_4, Na_2SO_4 and $ZnSO_4 \cdot H_2O$ in the correct ratios. The abilities of each form of the ternary composition to retard smoke formation in the model PVC compound were determined using the NBS Smoke Chamber test. The comparative results from the NBS Smoke Chamber test are given in Table VI. These results clearly show that in this laboratory combustibility test, equivalent amounts of the three different forms of the ternary glass composition gave essentially equivalent degrees of smoke reduction in the model PVC compound.

3.6. Preparation of transition metal-modified sulphate glasses

The experimental objective was to modify the composition of the ternary sulphate Glass 3 (Table II) in order to obtain glass-forming melts with higher viscosities relative to Glass 3. This was attempted by adding one or more additional metal sulphates to the ternary glass composition. The rationale was either to substitute them in part for the $ZnSO_4$ component or to add them to combinations of the known low-melting ternary and binary eutectic compositions. This is a well-known approach in the glass manufacturing industry for synthesizing low-melting glasses. Sulphates of aluminium, cadmium, cerium, copper, manganese, nickel and vanadium were investigated as additives to the ternary glass composition. The most promising metal sulphate additives were those of copper, manganese,

TABLE VI NBS Smoke Chamber comparison of different forms of the ternary composition 3 in PVC

Additives (phr)				D_m/g^*	Smoke decrease[†] (%)
Ternary Glass 3	Glass 3, devitrified	Glass 3, components	MoO$_3$		
—	—	—	—	79 ± 2	—
—	—	—	5	24 ± 3	70
10	—	—	—	26 ± 1	67
—	10	—	—	26 ± 6	67
—	—	10	—	29 ± 2	63
10	—	—	5	20 ± 4	75
—	10	—	5	20 ± 3	75
—	—	10	5	19 ± 2	76
40	—	—	—	19 ± 2	76
—	40	—	—	18 ± 4	77
—	—	40	—	19 ± 0	76
40	—	—	5	10 ± 1	87
—	40	—	5	9 ± 2	89
—	—	40	5	8 ± 1	90

*NBS Smoke Chamber smoke number per gram of sample tested.
†Percentage decrease in smoke relative to the control (no additives).

TABLE VII Preparation of transition metal-modified zinc sulphate glasses

Identification	Component sulphates	Composition (mol %)	Temperature (°C)	Melt	Glass*
TM–1	K_2SO_4 Na_2SO_4 $ZnSO_4$ $NiSO_4$	25 25 25 25	560	Viscous, brown	Yellow-orange glass–ceramic
TM–2	K_2SO_4 Na_2SO_4 $ZnSO_4$ $NiSO_4$	17.6 23.5 47.1 11.8	560	Brown	Yellow-orange glass + glass–ceramic
TM–3	K_2SO_4 Na_2SO_4 $ZnSO_4$ $MnSO_4$	22.2 11.1 44.4 22.2	560	No melting (pink-white)	–
TM–4	K_2SO_4 Na_2SO_4 $ZnSO_4$ $CuSO_4$	17.6 23.5 47.1 11.8	560	Clear blue- green	Transparent blue-green
TM–5	K_2SO_4 Na_2SO_4 $ZnSO_4$ $VOSO_4$	17.6 23.5 47.1 11.8	560	Clear dark green	Transparent dark purple

*These results are for melts which were quenched by pouring them on to a polished aluminium plate at dry-ice temperature.

nickel and vanadium, all first-row transition metals. Although the manganese compositions did not melt at the selected 560° C melt-forming temperature, they were interesting because they appeared to form homogeneous crystalline solids. The five transition metal (TM)-modified compositions selected for evaluation in the rigid PVC model compound are described in Table VII.

As shown in Table VII, the compositions containing copper and vanadium were readily quenched into colourful, transparent glasses. The similar melting and glass-forming characteristics of these two compositions, TM–4 and TM–5, is not surprising, since the vanadyl (VO^{2+}) and Cu^{2+} ions have very similar electronic and chemical properties. Both of the nickel-containing compositions, TM–1 and TM–2, formed very homogeneous glass–ceramic compositions. And, as mentioned before, TM–3, the manganese-containing composition, formed a homogeneous crystalline solid with a pink tint. All of the solid TM

sulphate products were readily ground into pigment-size powders.

3.7. Processing characteristics of TM-modified sulphates

All five of the selected modified sulphate compositions were readily incorporated into the organotin-stabilized model PVC compound. As in the case of ternary Glass 3, all of the PVC compounds were translucent. However, two of the PVC compounds did not reflect the colour of the sulphate additive. These were the compounds containing the TM–4 copper glass and the TM–5 vanadyl glass. The light blue copper glass gave rise to tan or brown PVC compounds. Based on additional studies, the brown colour appears to result from an interaction between Cu^{2+} ions in the glass and the tin stabilizer. The light purple TM–5 vanadyl glass resulted in green PVC compounds. Since VO^{2+} and Cu^{2+} ions have similar chemical properties, it is likely the green colouration also results

TABLE VIII NBS Smoke Chamber evaluation of PVC containing low levels of transition metal-modified sulphate compositions

TM–1 (Ni ceramic)	TM–2 (Ni ceramic)	TM–3 (Mn solid)	TM–4 (Cu glass)	TM–5 (VO glass)	MoO_3	D_m/g*	Smoke decrease† (%)
—	—	—	—	—	—	71 ± 4	—
—	—	—	—	—	5	27 ± 2	62
10	—	—	—	—	—	33 ± 4	52
10	—	—	—	—	5	19 ± 1	73
—	10	—	—	—	—	28 ± 1	60
—	10	—	—	—	5	19 ± 1	73
—	—	10	—	—	—	32 ± 4	55
—	—	10	—	—	5	17 ± 0	76
—	—	—	10	—	—	25 ± 3	65
—	—	—	10	—	5	15 ± 2	79
—	—	—	—	10	—	26 ± 2	63
—	—	—	—	10	5	18 ± 3	75

Additives (phr)

*NBS Smoke Chamber Smoke Number per gram of sample tested.
†Percentage decrease in smoke relative to the control (no additives).

TABLE IX NBS Smoke Chamber evaluation of PVC containing high levels of transition metal-modified sulphate compositions

Additives (phr)						D_m/g*	Smoke decrease[†] (%)
TM-1 (Ni ceramic)	TM-2 (Ni ceramic)	TM-3 (Mn solid)	TM-4 (Cu glass)	TM-5 (VO glass)	MoO₃		
—	—	—	—	—	—	76 ± 2	—
—	—	—	—	—	5	28 ± 3	63
40	—	—	—	—	—	20 ± 0	74
40	—	—	—	—	5	10 ± 1	87
—	40	—	—	—	—	17 ± 0	78
—	40	—	—	—	5	10 ± 2	87
—	—	40	—	—	—	20 ± 5	74
—	—	40	—	—	5	10 ± 0	87
—	—	—	40	—	—	17 ± 4	78
—	—	—	40	—	5	8 ± 0	89
—	—	—	—	40	—	13 ± 1	83
—	—	—	—	40	5	7 ± 0	91

*NBS Smoke Chamber Smoke Number per gram of sample tested.
[†]Percentage decrease in smoke relative to the control (no additives).

from an interaction between VO^{2+} ions and the tin stabilizer.

3.8. NBS Smoke Chamber evaluation of TM-modified sulphates

The NBS Smoke Chamber evaluation of the PVC compounds containing the TM-modified sulphate compositions is summarized in Tables VIII and IX. The data show that all the modified sulphate glasses are effective smoke retarders in PVC compounds at both 10 and 40 phr levels. Like the precursor ternary Glass 3, the transition metal sulphate-modified glasses also act in concert with MoO_3 to provide extremely effective smoke-retarders systems for PVC.

An examination of Tables VIII and IX reveals that the two most effective TM sulphate smoke retarders are the TM-4 copper glass and the TM-5 vanadyl
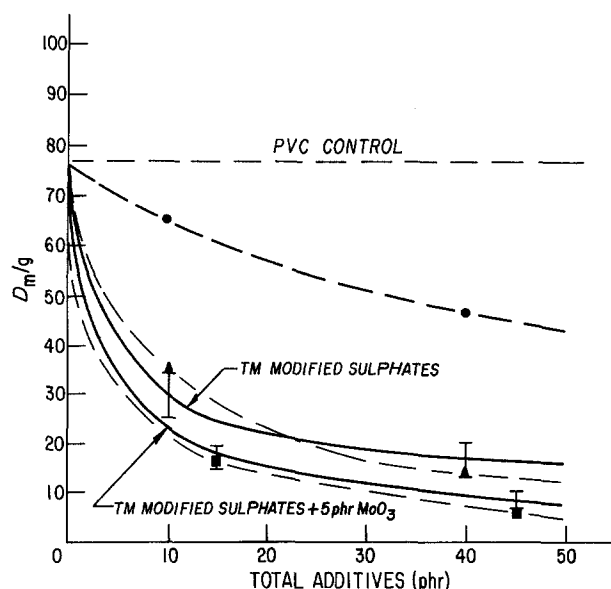

Figure 3 Efficacy of the transition metal-modified sulphate compositions as smoke-retarder additives. D_m/g is the Smoke Number from the NBS Smoke Chamber Test in the flaming mode. Comparative data from ternary sulphate Glass 3 and BaSO₄ (an "inert" diluent) are also presented. The two TM-modified sulphate curves include data from all of the TM compositions shown in Tables VIII and IX. (●) BaSO₄, (▲) ternary Glass 3, (■) ternary Glass 3 + MoO₃.

glass. This is consistent with copper compounds being the most effective class of smoke and fire retarder additives for rigid PVC [1], and with VO^{2+} behaving chemically like Cu^{2+}. However, for all practical purposes there is not much to choose from between any of the TM sulphate additives. In addition, a comparison between Tables III and IV and Tables VIII and IX shows that the ternary sulphate glasses and the TM-modified sulphate glasses are essentially equally effective as smoke retarders for PVC. This is graphically illustrated in Fig. 3 where all of the TM sulphate data at a given concentration level are averaged together and shown on one curve, with error bars expressing the spread in the data.

3.9. Smoke-Char Test evaluation of TM-modified sulphates

The smoke-reducing and char-forming properties of the TM-modified sulphate compositions were determined using the Smoke-Char Test. Summaries of the results along with results from ternary Glass 3 are presented in Tables X and XI. The smoke-reducing properties of the TM sulphate compositions closely paralleled the results obtained using the NBS Smoke Chamber. The relationship between the two different Smoke Numbers, D_m/g (NBS) and S_{PVC} (Smoke-Char), is depicted in Fig. 4. Included in Fig. 4 are data points taken from the ternary base sulphate Glass 3 before and after crystallization. The data in Fig. 4 were subjected to a linear regression analysis which gave

$$D_m/g = 0.2469\ S_{PVC} + 6.8293$$

with a regression coefficient of 0.9164. Thus there is a linear dependence between D_m/g and S_{PVC}. But the plot in Fig. 4 shows there are utilitarian limitations to the linear dependence. Because of the scatter of the experimental data, the Smoke-Char Test will not give a reliable ranking of the performance of PVC compounds containing sulphate glasses over a narrow spread (e.g. 5 units) of D_m/g. However, the Smoke-Char Test is shown to be a useful laboratory screening test for predicting which PVC–sulphate glass combinations will have either high or low Smoke Numbers in the NBS Smoke Chamber Test.

TABLE X Smoke-Char evaluation of PVC containing low levels of low-melting sulphate compositions*

Additives (phr)							S_{PVC}[†]	Smoke decrease[‡] (%)	%BC[§]
Ternary Glass 3	TM-1 (Ni ceramic)	TM-2 (Ni ceramic)	TM-3 (Mn solid)	TM-4 (Cu glass)	TM-5 (VO glass)	MoO₃			
—	—	—	—	—	—	—	113	—	1.9
10	—	—	—	—	—	—	76	33	28
10	—	—	—	—	—	5	41	64	45
—	—	—	—	—	—	5	83	26	33
—	10	—	—	—	—	—	96	15	20
—	10	—	—	—	—	5	65	42	46
—	—	10	—	—	—	—	83	26	34
—	—	10	—	—	—	5	38	66	53
—	—	—	10	—	—	—	92	18	29
—	—	—	10	—	—	5	60	47	44
—	—	—	—	10	—	—	68	40	37
—	—	—	—	10	—	5	36	68	53
—	—	—	—	—	10	—	63	44	38
—	—	—	—	—	10	5	29	74	57

*For S_{PVC} and %BC the standard deviation is within 20% of listed values.
[†]Smoke-Char Smoke Number per gram of PVC in sample.
[‡]Percentage decrease in smoke relative to the control (no additives)
[§]Percentage of the hydrocarbon part of the PVC converted to char.

The Smoke-Char data in Tables X and XI clearly show that the PVC compounds which gave the least smoke also gave the most char. However, there is no linear dependence. But there is an exponential relationship between the smoke formed in the Smoke-Char Test (S_{PVC}) and the percentage of hydrocarbon backbone of the PVC which was converted into char (%BC). This relationship is shown in Fig. 5. The linear dependence between log S_{PVC} and %BC was calculated to be

$$\log S_{PVC} = -0.0189\ \%BC + 2.4543$$

with a regression coefficient of 0.9245.

3.10. Torch Test evaluation of TM-modified sulphates

All of the PVC compounds containing the TM-modified sulphates were burned in the Torch Test. The results are summarized in Table XII. At the 10 phr level, the TM-modified sulphates gave less thermal protection than their base composition, the ternary sulphate Glass 3 (see Table V). The same result was observed when the TM sulphates at a loading of 10 phr were combined with 5 phr MoO₃. At the 40 phr filler level of loading, the nickel-modified TM-1 glass–ceramic outperformed the other TM sulphate compositions, including the ternary Glass 3.

The outstanding thermal protection afforded by the TM-1 nickel-modified sulphate is probably the result of its high viscosity, which persists at temperatures well above the 560° C melting temperature used in its formation. Just before the TM-1 containing PVC samples failed in the Torch Test, the central region of the large intumescent char changed colour from black to a light yellow-green. Concurrently with this colour change, the char became soft and lost its structural integrity. This permitted the temperature of the back side of the test specimen to rise quickly and exceed the

TABLE XI Smoke-Char evaluation of PVC containing high levels of transition metal-modified sulphate compositions*

Additives (phr)							S_{PVC}[†]	Smoke decrease[‡] (%)	%BC[§]
Ternary Glass 3	TM-1 (Ni ceramic)	TM-2 (Ni ceramic)	TM-3 (Mn solid)	TM-4 (Cu glass)	TM-5 (VO glass)	MoO₃			
—	—	—	—	—	—	—	98	—	11
40	—	—	—	—	—	—	53	46	34
40	—	—	—	—	—	5	23	77	55
—	—	—	—	—	—	5	65	34	37
—	40	—	—	—	—	—	71	28	28
—	40	—	—	—	—	5	23	76	56
—	—	40	—	—	—	—	39	60	41
—	—	40	—	—	—	5	20	80	52
—	—	—	40	—	—	—	37	62	46
—	—	—	40	—	—	5	21	79	69
—	—	—	—	40	—	—	30	69	40
—	—	—	—	40	—	5	12	88	66
—	—	—	—	—	40	—	22	78	51
—	—	—	—	—	40	5	8	92	74

*For S_{PVC} and %BC the standard deviation is within 20% of listed values.
[†]Smoke-Char Number per gram of PVC in sample.
[‡]Percentage decrease in smoke relative to the control (no additives).
[§]Percentage of the hydrocarbon part of the PVC converted to char.
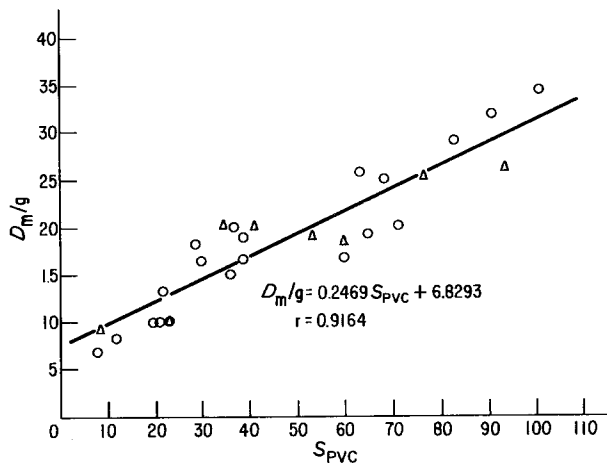
Figure 4 Comparison of the NBS Smoke Chamber (flaming mode) Smoke Number (D_m/g) with the Smoke-Char Smoke Number (S_{PVC}). (O) = TM-modified sulphate compositions; (△) ternary base sulphate Glass 3 and crystallized ternary Glass 3.
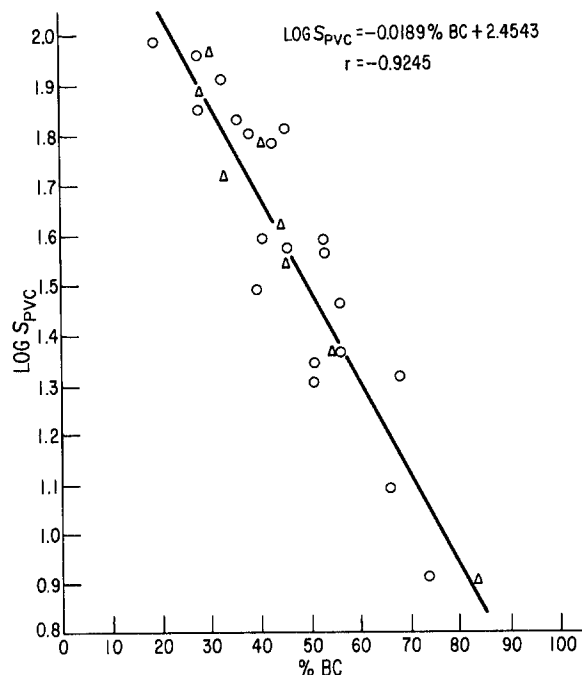

Figure 5 The relationship between smoke reduction and char formation in a PVC compound containing sulphate smoke retarders. S_{PVC} is the Smoke Number and %BC is the percentage of hydrocarbon backbone of the PVC which is converted into char in the Smoke-Char Test. (O) TM-modified sulphate compositions; (△) ternary sulphate Glass 3 and crystallized ternary Glass 3.

250° C test limit. X-ray diffraction analysis of the char residue revealed that its two main crystalline components were NiO and Ni_2O_3. I conclude that failure occured when the protective liquid sulphate thermally decomposed. In turn, this permitted the char to oxidize and lose its ability to act as a thermal barrier. In general, PVC containing TM-modified sulphates showed modest to large intumescence effects in the Torch Test. The intumescence was also accompanied by the formation of hard, structurally intact chars. The preceding two observations also applied to PVC compounds containing mixtures of the TM sulphates with MoO_3. Unfortunately, the measured protection time in the Torch Test does not reflect the intumescence character of the heated PVC samples. This is because the sudden failure observed for all but the

PVC samples containing the nickel-modified sulphate additives resulted from the hard barrier char suddenly developing a large crack, which permitted the impinging flame to penetrate the intumescent test specimen. This sudden, unpredictable cracking of the barrier char also explains the severe reproducibility problems encountered with the Torch Test.

TABLE XII Torch Test evaluation of PVC containing the transition metal-modified sulphate compositions

Additives (phr)						Protection Time* (sec)
TM–1 (Ni ceramic)	TM–2 (Ni ceramic)	TM–3 (Mn solid)	TM–4 (Cu glass)	TM–5 (VO glass)	MoO_3	
—	—	—	—	—	—	51 ± 17
—	—	—	—	—	5	266 ± 193
10	—	—	—	—	—	90 ± 35
—	10	—	—	—	—	43 ± 9
—	—	10	—	—	—	53 ± 17
—	—	—	10	—	—	124 ± 14
—	—	—	—	10	—	72 ± 58
10	—	—	—	—	5	214 ± 47
—	10	—	—	—	5	58 ± 26
—	—	10	—	—	5	272 ± 41
—	—	—	10	—	5	121 ± 8
—	—	—	—	10	5	88 ± 44
40	—	—	—	—	—	882 ± 46
—	40	—	—	—	—	121 ± 13
—	—	40	—	—	—	362 ± 308
—	—	—	40	—	—	172 ± 118
—	—	—	—	40	—	84 ± 21
40	—	—	—	—	5	381 ± 190
—	40	—	—	—	5	91 ± 60
—	—	40	—	—	5	166 ± 98
—	—	—	40	—	5	269 ± 154
—	—	—	—	40	5	86 ± 13

*Time for the back of the sample to reach 250° C.

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