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Polymer-Bonded Coloured Smoke Compositions

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Polymergebundene Farbrauchsätze

Polymergebundene Farbrauchsätze bringen zahlreiche Vorteile gegenüber den konventionellen gepreßten Rauchsätzen, wie z. B. verbesserte mechanische Eigenschaften und sichere Handhabung. Das Defense Research Establishment Valcartier (DREV) hat gießbare Farbrauchsätze entwickelt unter Verwendung eines bekannten hydroxy-terminierten Polybutadien-Prapolymeren, das mit einem handelsüblichen Diisocyanat ausgehärtet wurde. Diese Rauchsatzmischungen enthalten die Bestandteile, wie sie üblicherweise in gepreßten Pulvermischungen verwendet werden, sie sind jedoch in einem Polymerbinder verteilt. Ein Farbstoffgranulat wird verwendet, um die niedrige Viskosität zu liefern, die verlangt wird für den Gießprozeß. Es werden sowohl die erforderlichen Bestandteile und die Herstellungstechnik beschrieben, als auch die Eigenschaften und Vorteile solcher Mischungen.

Compositions fumigènes colorées à liant plastique

Les compositions fumigènes colorées à liant plastique offrent, par rapport aux compositions fumigènes classiques, réalisées par pressage, de nombreux avantages, tels que de meilleures propriétés mécaniques et une sécurité de manipulation accrue. Le Centre de Recherches pour la Défense Valcartier (CRDV) a mis au point des compositions fumigènes coulables en utilisant un polybutadiène prépolymérisé avec des radicaux hydroxyles en bout de chaînes et un diisocyanate du commerce comme agent polymérisant. Ces compositions fumigènes contiennent les mêmes substances que les compositions obtenues par pressage, mais celles-ci sont réparties dans une matrice en polymère. On utilise un granulat de colorant pour que la masse ait une viscosité suffisamment faible afin de pouvoir être coulée. On décrit les différents composants, les techniques de préparation, les propriétés et les avantages de telles compositions.

Summary

// Polymer-bonded smoke compositions offers numerous advantages over conventional pressed smoke mixtures such as improved mechanical properties and safety in handling. The Defense Research Establishment Valcartier (DREV) has developed pour-castable coloured smoke compositions using a well known hydroxy-terminated polybutadiene prepolymer cured with a commercially available diisocyanate. These smoke formulations consist of ingredients typically found in pressed powder mix, but dispersed in a polymeric binder. A granulated dye is utilized to provide the low viscosities required for pour-casting. The necessary ingredients and processing techniques as well as the properties and inherent advantages of such compositions are described. //

1. Introduction

Smoke generators have a tactical use primarily as signalling devices in ground-to-ground and ground-to-air communication. Alternatively they may serve as wind-drift indicators or target identification markers. Coloured smokes are generally produced by gradually evaporating dyestuff from a mixture of dye and a pyrotechnic heat source composed of potassium chlorate and powdered sugar or sulfur as the oxidizer/fuel mixture and sodium or potassium bicarbonate as a coolant and stabilizing agent.

The pour-castable coloured smoke compositions developed at DREV consist of ingredients typically found in pressed compositions. The difference, however, is that these ingredients are now dispersed in an elastomeric binder. DREV's involvement in the field of castable smoke compositions started[1] in 1971. Preliminary results were encouraging but inclusion of a binder did not assure the castability of the compositions. The substitution of commercial dye with a granulated material made possible the preparation of true pour-castable compositions[1]. After development of a granulation process for organic dyes[2,3], DREV was in a position to undertake the development of smoke generators based on pour-castable pyrotechnic compositions[4].

2. Description of Ingredients

2.1 Formulations

The coloured smoke compositions dealt with herein consist primarily of an organic dye, potassium chlorate, lactose or sulfur and sodium bicarbonate dispersed in an elastomeric binder. The range of concentrations experimented, during development, for each of these ingredients is presented in Table 1.

The compositions were developed to generate five colours of smoke: red, violet, green, yellow and orange. Other colours may be obtained by choosing the desired dye mix and adjusting the formulation accordingly to yield desirable processing and performance characteristics[5]. While fast burning compositions can be ignited by a sensitized primer sheet alone, the slow burning compositions required to achieve a long smoke emission duration are more difficult to ignite. An ignition smoke composition is therefore required, containing typically less dye and more oxidizer/fuel mixture than the compositions described in Table 1. This oxidizer-rich composition, which is easier to ignite and burns faster, provides a rapid smoke buildup when subjected to the hot flame of a sensitized primer sheet. While producing an acceptable amount of smoke, it transfers heat to the main smoke composition that gradually takes over.

Table 1. Range of Concentrations of Ingredients in Coloured Castable Smoke Compositions

Ingredients	Range of Concentration [% by weight]
Granulated dye	38–46
$KClO_3$	22–28
S or lactose	4–9
$NaHCO_3$	2–19
Binder	17–20

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2.2 Organic dyes

Commercially available organic dyes, if used as supplied (particle size 10 μm–15 μm), produce compositions with excessive viscosities, and pour-casting is no longer possible. It is well known however, that the viscosity of a liquid/solid suspension is closely related to the particle size distribution of the solids. By optimizing the ratio of fine versus large particles, a minimum viscosity can be obtained. Because the dye forms the main portion of the solids, the use of a granulated dye is essential to maintain the low viscosities required for pour-casting. Since dye granules in the desired size range were not commercially available, a granulation process was developed[2,3]. The commercial dyes successfully granulated and used in smoke formulations include 1-amino-anthraquinone, 1-methylamino-anthraquinone, Smoke Yellow 6, Smoke Yellow 33 and Smoke Green 4.

The granulated dyes used in the smoke compositions have a mean particle size in the range of 500 μm–700 μm. A typical particle size distribution is given in Fig. 1. Tests have shown that when finer or narrower distributions are used, higher end-of-mix viscosities and ignition delay problems are observed.

2.3 Oxidizer

The oxidizer is a crystalline potassium chlorate with a mean particle size of 35 μm. Because the oxidizer is the ingredient with the greatest influence on the burning rate of the composition, its particle size must be strictly controlled, and it must be kept free flowing by means at an anticaking agent such as tricalcium phosphate.

2.4 Fuel

Sulfur, in the form of sublimed powder, is the preferred fuel in these formulations because the colour quality of the smokes produced, particularly with the red and green compositions, is significantly inferior with lactose. A stoichiometric ratio between the oxidizer and the fuel (2.55:1 for the case of $KClO_3$ and S) is not readily apparent from Table 1, as the binder also partially serves as a fuel.

2.5 Coolant

Sodium bicarbonate (USP Standard grade) serves principally as a coolant but also as a gasifying and stabilizing agent. It acts as a scavenger for oxidizing species and in this capacity tends to retard degradation of the dye caused by oxidation or pyrolysis. Furthermore, its presence reduces the possibility of flaming. When compared with pressed compositions, the proportion of $NaHCO_3$ is relatively low. The difference, however, is once again explained by the binder, which also serves as a coolant.

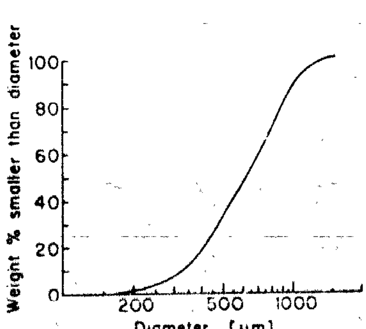

Figure 1. Typical particle size distribution for granulated dye.

2.6 Binder

In castable smoke compositions, it is the binder that serves as the medium in which all the solids are dispersed and, once properly cured, maintains the integrity of the smoke grain. The binder used at DREV is based on a hydroxy-terminated polybutadiene (HTPB), with which good results had been achieved during a previous development program of composite rocket propellants. Its formulation typically consists of 56.9% by weight of R-45 HT (ARCO Chemical Co.), including 1% by weight of AO-2246 antioxidant (American Cyanamid), plasticized with 25% by weight of isodecyl pelargonate (IDP, Emery Industries) and cured with 18.1% by weight of dimeryl diisocyanate (DDI-1410, General Mills). In this formulation, the ratio of cyanate end-groups of the curing agent to the hydroxyl radicals provided by the polymer (NCO/OH) is 1.2:1. An excess of curing agent is necessary as a certain amount is consumed by the dye[5]. Each different dye, however, does not consume the same proportion of isocyanate and therefore, certain modifications have to be made to the binder formulation to achieve a more even curing rate.

3. Processing

3.1 Dye granulation

A high capacity granulation process was developed at DREV between 1974 and 1978[2,3]. This continuous process involves only ambient temperature mechanical operations and economically produces dye granules, using equipment readily available in the industry, in substantially any desired size range with a minimum of fine powder.

The process includes a compactor, a grinder, a separator and a dust collector. Finely divided, commercially available organic dye material is fed from a feed-hopper into the nip of a pair of rolls in the compactor. The laminar product, which is normally 1 cm^2 to 5 cm^2 in area and 0.5 mm to 1.3 mm thick depending upon the specific dye and roll settings, is then fed to a relatively slowly rotating hammer mill, which produces particles typically in the range 10 μm to 2000 μm, depending upon the shape and size of the holes in the grid in the crushing chamber. The discharge from the mill passes into a vibrating screen separator and the proper size fraction is retained. The undersized material is recycled with the fines from the dust collector.

3.2 Mixing

The smoke composition is prepared according to a mixing cycle, which was established with the aid of thermal analysis techniques to avoid, as much as possible, hazardous combinations of ingredients. The prepolymer, including the antioxidant and the plasticizer, is first poured into the mixer. The $NaHCO_3$ and the sulfur or lactose are then added and mixed for 10 min at atmospheric pressure with the mixer temperature maintained at 60 °C. Then, the granulated dye is added and mixing continued for a further 10 min. The $KClO_3$ is added to the other ingredients and mixing continued for 5 min at atmospheric pressure. After this the vacuum is applied and mixing continued for 45 min at 60 °C.

This mixing cycle was used with an Atlantic Research helicone vertical mixer that was operated forward during the entire mix. While this type of mixer was used during the development program, the low viscosities of the formulations permit the use of other types of jacketed mixers.

3.3 *Casting and curing*

At the end of the mixing cycle, the composition is cast under vacuum, in transfer tubes. These are then placed in a press and the proper amount of composition is loaded into each container. It is also possible to cast directly from the mixer into the individual grenades (or other store), either under vacuum or at atmospheric pressure. Mandrels of suitable shape, coated with an appropriate release agent, are then inserted into the store container, expelling any excess composition and forming the interior core cavity. The composition is then cured for 5 days at 60 °C, after which the mandrel is removed and the store into which the composition has been cast is ready for final assembly.

4. Properties

4.1 *Processing properties*

To achieve pour-castable formulations, the end-of-mix (EOM) viscosity should be no greater than 10 kP (1 kPa · s) and preferably 5 kP, but not so low that settling out of solids could be a problem during casting and curing. Compositions with viscosity as low as 1 kP have been cast without any settling problems.

The pot-life, defined here as the period between the initial addition of the polymerizing agent (DDI) and the time the viscosity reaches 10 kP at 60 °C, should be at least 1 to 4 hours to permit time for loading the batch into containers. Typical processing properties of six batches are shown in Table 2.

The end-of-mix (EOM) viscosities were obtained with a Brookfield apparatus model HAT mounted on a Helipath stand. All the measurements were made with a type D spindle at a rotational speed of 2.5 r/min and a casting temperature of 60 °C. Pot-life data were taken with the Rotovisko apparatus (Gebrüder Haake, Berlin) coupled with special controls for continuous recording of the torque and automatic retracting of the viscometer probe.

Table 2. Typical Processing Properties of Castable Smoke Compositions

Colour	Binder Content [% by weight]	EOM Viscosity [kP]	Pot-life [h]
Red	20	5.1	3.0
Violet	20	1.3	8.5
Green	20	1.9	10.0
Yellow	20	2.5	9.0
Orange	18	2.2	9.5
Orange[a]	18	1.8	10.0

[a] Ignition smoke composition.

Table 3. Typical Mechanical Properties of Castable Smoke Compositions

Colour	Maximum Tensile Strength [kPa]	Elongation at Maximum Strength [%]	"Shore A" Hardness
Violet	760	22	59
Red	720	13	64
Green	650	18	58
Yellow	950	14	70

4.2 *Mechanical properties*

After a normal curing period of five days at 60 °C, cast blocks were X-rayed and cut into slabs 1.27 cm thick. JANNAF dog-bones were die-cut and tensile tests conducted at 23 °C on an Instron Tester at an extension rate of 5 cm/min. Typical results are shown in Table 3, each figure is a mean value established from six samples. The desirable properties at 23 °C for the smoke compositions are specified as a minimum "Shore A" hardness of 25, a tensile strength of not less than 300 kPa with at least 10% elongation.

4.3 *Burning rate*

With fast burning compositions, sensitized primer sheet top-ignited cylindrical smoke grains are used to determine the burning rate[5]. It varies from 1.0 cm/min for an ignition smoke composition to 2.0 cm/min for a fast composition used in a signalling grenade. Slow burning compositions, used for long emission time, show burning rates as low as approximately 0.3 cm/min judging from the burning time of actual generators. The whole spectrum of burning rates can be covered by varying the ratio of dye to fuel/oxidizer mixture. The proportion of sodium bicarbonate will also affect the burning rate.

To speed up the combustion and augment the smoke volume without major increases in combustion temperature, small quantities (up to 2% or 3%) of a combustion catalyst may be incorporated into the smoke composition[1–4]. Iron oxide has been found to be a particularly suitable combustion catalyst. When sulfur is used as a fuel, the burn rate is generally sufficiently high so that a combustion catalyst is not needed.

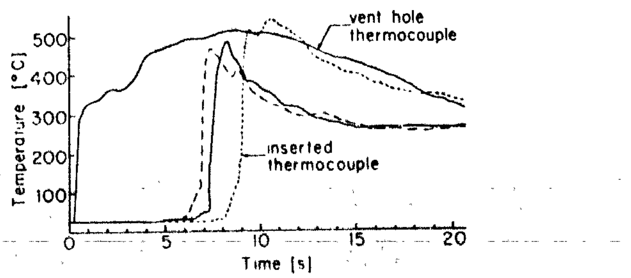

Figure 2. Typical recording of thermocouple positioned at the vent hole or in the smoke grain of a grenade filled with castable composition.

4.4 Burning temperatures

Chromel-alumel thermocouples, positioned at the vent hole or inserted into the smoke grain, were used to record burning and exhaust gas temperatures of castable smoke composition used in signalling smoke grenades[5]. A typical recording is shown in Fig. 2. All the maximum temperatures recorded were in the range 430 °C–597 °C and are comparable to those of pressed compositions.

4.5 Safety classification

All the smoke compositions used in actual smoke generators were tested by the Canadian Explosives Research Laboratory (CANMET, Bells Corners, Ontario) of Energy, Mines and Resources Canada. The classification is identical for each smoke composition:
Canadian Explosives Act: Class 4, Division 2
Transport: Class B
Safety Distance: X
United Nations: 1.3 G

4.6 Advantages of castable compositions

Castable smoke compositions possess a number of inherent advantages over conventional pressed compositions. Among these, are:

- improved mechanical properties and stability: the susceptibility of such mixtures to shock and deterioration is decreased.
- improved safety in handling: because of the wet processing technique, the processing personnel have a reduced exposure to dust, and the risks arising from explosive dust are minimized. The compositions are also less sensitive to ignition by impact, friction or electrostatic discharge.
- improved performance: the fact that the pyrotechnic mixture is well dispersed means that it burns at a more uniform rate, and with more uniformity from one generator to another.
- greater flexibility in grain design: the smoke composition can be very easily cast in a variety of configurations, and is not restricted solely to cylindrical shapes. This is especially advantageous for the filling of aerodynamically-shaped projectiles.
- suitability for mass production using an automated production line. There is no need for incremental filling techniques.

4.7 Current applications

The developed compositions have found applications into smoke generators such as the 35-s signalling grenade. The design has been accepted for use by the Canadian Forces and production contracts have been awarded to private industry. The contractor, with previous experience in conventional pressed compositions, has indicated that the processing of castable smoke compositions is actually easier, faster and safer than the conventional pressed compositions. The performance of the grenade has been evaluated by the user as a considerable improvement over existing stores in inventory. Another example of the improvement that can be obtained with a castable composition is the case of a free-fall 3-min marker launched from helicopters. A castable composition has been loaded into the older model marker originally filled with a pressed composition. Although the total weight of the new model is the same, the volume of smoke emitted over a 3-min period was considerably increased. The marker has been successfully subjected to environmental testing to further qualify the design. Finally, a long burning 12-min marker employing a pour-castable smoke composition is presently under development at DREV.

5. Conclusions

By the application of existing technology, associated with composite propellants, the Defense Research Establishment, Valcartier (DREV) has successfully developed pour-castable coloured smoke compositions using a binder based on a commercially available polybutadiene prepolymer. These compositions have an end-of-mix viscosity below 5 kP to enable casting by gravity alone. The realization of true castable products was made possible by the development of a high capacity process to achieve granulation in a satisfactory manner. The substitution of a commercial dye with a granulated material having an average particle size of 500 μm–700 μm has provided a solution to the problem of high viscosity.

These polymer-bonded pour-castable smoke compositions have been successfully loaded into operational smoke generators presently in production for the Canadian Forces and also into experimental smoke markers still under development.

6. References

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