

The present invention concerns pyrotechnical smoke compositions which produce smoke impenetrable in the visible and infra-red range.

Artificial smokes are produced in the technology
5 on the one hand in order to keep frost away from plantations (especially fruit and vine cultures). There is thereby usually produced either smoke or oil mist or a fine water mist is sprayed which can additionally be stabilised by glycerol, fatty alcohols or the like and
10 is spread out over the cultures to be protected in a more or less thick layer in order to reflect warmth irradiated from the ground and thereby to prevent a cooling. According to the purpose, these mists or clouds must be maintained for comparatively long periods
15 of time, i.e. the loss due to condensing out and wind movement must be supplemented by continuous replacement. Therefore, for this purpose, continuously operating equipment are usually employed.

Artificial smokes find a further use especially in
20 the military sector for the camouflaging of equipment, troop divisions and vehicles. Especially in the case of the protection of troop divisions and vehicles, it is thereby important to remove these from a direct observation by the opponent for a short time, for which
25 purpose a pyrotechnical charge is usually fired in the direction of the opponent which divides up like a shrapnel shell and produces a plurality of smoke-producing particles which provide for a very rapid and uniform smoke screening of comparatively large areas
30 (cf. DE-AS 30 31 369 and the literature there cited).

For this purpose, there are known a large number of different smoke and mist mixtures. For example, there may be mentioned titanium tetrachloride, silicon tetrachloride, chlorosulphonic acid or their combinations with ammonia or sulphur trioxide as liquid smoke
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formers or red phosphorus, HC mixtures (hexachloro-ethane/zinc/zinc oxide) and ammonium perchlorate/zinc oxide as solid smoke formers. In the case of use, these materials are converted into smoke either by a secondary
5 combustion reaction or by appropriate products liberated by their reaction with one another. Decisive for the quality of the smoke formation is the speed of the formation, the concentration and the nature of its spreading out, as well as the period of the smoke screening.
10 Suitable smoke mixtures are already known for all these purposes (cf. DE-AS 30 31 369).

See e.g. DE-OS 25 56 256, DE-OS 25 09 539, DE-OS 18 12 027, DE-AS 12 46 488, DE-OS 30 12 405, DE-OS 27 29 055, DE-OS 27 43 363, DE-OS 19 13 790.

15 However, for a wide use in modern defence technology, these mixtures have a quite important disadvantage. Whereas previously it was especially important to produce a smoke which was as dense as possible in visible light, military observers today
20 additionally have available infra-red direction and heat picture apparatus which utilise the fact that military targets, because of their energy exchange, emit very intensive heat radiation which is detectable at great distances. Since, due to atmospheric components, such
25 as CO₂ and water vapour, the infra-red radiation of certain wavelengths is selectively absorbed, these apparatus preferably operate in the so-called "windows" of the atmosphere which lie at 0.7 - 1.5 $\mu\text{m.}$, 2 - 2.5 $\mu\text{m.}$, 3 - 5 $\mu\text{m.}$ and 8 - 12 $\mu\text{m.}$ One endeavours
30 especially to operate in the 8 - 12 $\mu\text{m.}$ range since, in this, these disturbances by smoke, vapour and normal mist assume a minimum. Therefore, it is the task of pyrotechnical smoke compositions conversely to ensure in this range an absorption or reflection of the IR
35 radiation which is as high as possible.

Furthermore, from EU-A 0 037 515, it is known to combine smoke from halogen donors/metal powders or phosphorus smoke with a further, secondary smoke of organic acids or microballoons in order to produce therewith larger agglomerates which also display a light absorption in the region of $>8 \mu\text{m}$. The alkali metal salts (sodium, potassium, lithium nitrate) used in these mixtures as oxidation agents bring about, inter alia, also a signal action (coloration of the flame) but they are not suitable for changing the infra-red absorption.

Furthermore, most pyrotechnical smoke compositions contain corrosive, toxic or strongly acidic components, such as phosphorus pentoxide, hydrochloric acid, sulphuric acid, titanium or zinc salts which are extremely harmful to humans and plants in the concentration occurring in the smoke. Therefore, by the addition of metal oxides, buffer substances and ammonium compounds, in most of today's smoke compositions one has taken care that the smoke produced is only as weakly acidic as possible or is neutral. Therefore, one task of the invention is so to modify the known smoke compositions that these as far as possible do not act acidically.

Surprisingly, these tasks are solved by the measures characterised in the claims, i.e. in that one adds to the per se known smoke compositions a sufficient amount of caesium compounds.

Due to this addition of caesium compounds, the transparency of the smoke with IR light, especially of infra-red light with wavelengths of 3 - 5 or 8 - 12 μm , is quite decisively reduced, whereby it could hitherto not be ascertained upon what this depends.

Since, as is known, caesium salts display no absorptions in the near infra-red range of up to 12 μm .,

which are to be attributed to oscillation in which the caesium ions participate (caesium halides display no oscillation, caesium nitrate only the oscillation of the nitrate group at $7.2\text{ }\mu\text{m.}$), a direct absorption of the IR light cannot come into question for the effect. Since the amounts used, referred to the amount of the total smoke composition, correspond on average to only 25% and, corresponding to the other smoke-forming components, are present in small amount, the increase of the particle number of the dispersed system also cannot be made responsible for the effect. Since, according to the previous observations, the rate of vertical descent and condensability of the smoke clouds formed does not differ from that of the corresponding smoke compositions without addition of caesium salts, an improvement of the scattering action of the particles produced also does not appear to be responsible for the effect. Under the assumption that for these particles, in first approximation, Stokes' Law applies, i.e. the rate of vertical descent is proportional to the square of the particle diameter, an enlargement of the particle diameter from $1\text{ }\mu\text{m.}$ in usual smoke compositions to $10\text{ }\mu\text{m.}$, which would be necessary for an effective scattering in the IR range of $8 - 12\text{ }\mu\text{m.}$, would mean an increase of the rate of vertical descent by a factor of 100. Therefore, further investigations remain to be carried out in order to find a satisfactory theory why the pyrotechnical smoke composition according to the invention displays a satisfactory density not only in the visible but also in the infra-red.

Furthermore, the present invention is also concerned with the task of increasing the smoke-yield of phosphorus-containing smoke compositions.

The metals magnesium and titanium usually employed lead to an ash content, after combustion of

the smoke compositions, of 60 - 70%.

Surprisingly, it is possible to increase the effectiveness of such smoke compositions in that, instead of magnesium and titanium, there is used a zirconium/nickel alloy, preferably with 70% zirconium and 30% nickel. The ash content of such compositions can thereby be lowered to 5%. Additions of boron act in the same direction and additionally improve the IR absorption.

By additions of ammonium chloride, the effectiveness can be additionally increased.

The great advantage of the previously described smoke compositions consists in that they are passively effective. This means that they display no inherent thermal effect and thus do not change the picture of the surroundings in infra-red viewing apparatus.

In the following Examples, a series of smoke-compositions according to the invention are compared with corresponding smoke compositions without the additive according to the invention.

Example 1

Ammonium perchlorate smoke.

1.7 kg. Ammonium perchlorate, 1.5 kg. zinc oxide, 0.8 kg. polychloroisoprene and 0.5 kg. ammonium chloride are pasted with a solution of 0.5 kg. dioctyl phthalate in 1 litre of methanol. The mixture is forced through a sieve with a mesh size of 0.3 - 0.5 mm. and dried on racks. The dried granulate is then pressed according to DE-AS 30 31 369 into pressed bodies of about 50 g. In each case, 20 g. of the pressed bodies are combined with an ignition composition according to Example 2 of DE-AS 30 31 369 in a synthetic resin or metal shell to give a shot.

The ignition composition has the following components: magnesium powder (1.2 kg.), iron phosphate

(0.9 kg.), amorphous boron (2.39 kg.), pulverised chloroparaffin (0.8 kg.) and gunpowder (4.71 kg.). The magnesium powder and the iron phosphate were pre-mixed; the chloroparaffin, dissolved in 2 litres of perchloroethylene, was added thereto and mixed. The amorphous boron was added thereto and the mixing process repeated for 5 minutes. As last component, there was added thereto the gunpowder, mixed with the other components for 10 minutes, dried and pressed at 1500 bar.

10 The same mixture as above is additionally mixed with 0.4 kg. caesium nitrate and worked up in the same way to pressed bodies with a weight of about 50 g. As above, in each case, 20 pressed bodies are combined with an ignition composition in a shell to give a shot.

15 For the assessment of the smoke action, 3 white plates heated to about 40°C. are placed on the ground at a distance of 10 m. and observed at a distance of 100 m. with infra-red and optical viewing apparatus at wavelengths of 10 μm ., 3.5 μm ., and 0.6 μm . Smoke shells of the above composition are shot with a propellant charge about 40 - 50 m. in front of the target where, within seconds, a 3 - 15 m. high and 25 - 40 m. wide and deep smoke wall is formed. At temperatures of 22°C. and a relative atmospheric humidity of 48%, there are determined the covering relationships set out in the following Table.

30 By very good is understood a covering of 95 - 100%, i.e. the target is no longer to be differentiated from the background. By good is understood a covering of 80 - 95%, i.e. the target is scarcely distinguishable. By moderate is to be understood a covering of 50 - 80%. By poor is to be understood a covering of less than 50% at which the target is still clearly distinguishable.

Table 1

covering relationships in the case of observation wavelength			
	0.6 μm .	3.5 μm .	10 μm .
perchlorate	good	poor	poor
5 perchlorate/CsNO ₃	very good	good	good

Example 2.

Hexachloroethane smoke.

2.5 kg. Hexachloroethane, 0.8 kg. zinc oxide,
0.4 kg. silicon powder, 0.3 kg. aluminium powder and
10 0.3 kg. amorphous boron are intensively mixed and
pasted in a kneader with 2 kg. of a 10% elastomer binder
solution in acetone. The mixture is worked up to
pressed bodies with the same process as in Example 1,
which are insulated by an additional coating of meth-
15 acrylic resin and combined according to Example 1 to
give smoke shells.

The same mixture as above is worked up in corres-
ponding manner to smoke shells but with the addition of
1 kg. of caesium nitrate.

20 The smoke action is determined according to
Example 1, whereby the results are contained in the
following Table 2. The smokes formed have a pH value
of about 5 - 7. The elastomer consisted of butadiene.
Polybutadiene can also be used.

Table 2

covering relationships in the case of observation wavelength			
	0.6 μm .	3.5 μm .	10 μm .
HC mixture	very good	moderate	moderate
HC/CsCl	very good	very good	very good

Example 3

Red phosphorus smoke.

0.65 kg. Red phosphorus, 0.15 kg. iron (III) oxide, 0.15 kg. aluminium powder and 0.15 kg. magnesium powder are kneaded with 0.2 kg. 10% elastomer binder and worked up to pressed bodies according to Example 1.

In the same way, mixtures which additionally contain 0.40 kg. caesium nitrate are worked up to pressed bodies.

The smoke action is determined according to Example 1, whereby the results are contained in the following Table 3.

Table 3

	covering relationships in the case of observation wavelength		
	0.6 μm .	3.5 μm .	10 μm .
phosphorus	very good	poor	poor
phosphorus/CsNO ₃	very good	very good	very good

Example 4

0.65 kg. Hexachloroethane, 0.2 kg. silicon powder and 0.15 kg. aluminium powder are mixed and pressed under weak pressure into a shell which is combined with a propellant and ignition composition.

In the same way, mixtures are worked up which additionally contain 0.01 - 0.10 kg. caesium chloride.

The following smoke effects are obtained:

Table 4

	covering relationships in the case of observation wavelength		
	0.6 μm .	3.5 μm .	10 μm .
HC smoke	good	moderate	moderate
HC-CsCl	very good	very good	very good

In the following Examples are given successful formulations.

Butadiene (polybutadiene) is used as binder.

Example 5

- 5 55% red phosphorus
- 23% caesium nitrate
- 12% zirconium/nickel alloy 70:30
- 10% butadiene

Example 6

- 10 55% red phosphorus
- 20% caesium nitrate
- 4% manganese powder
- 6% zirconium/nickel alloy 70:30
- 5% fine aluminium powder
- 15 10% butadiene

Example 7

- 27% NH_4ClO_4
- 8% Zr/Ni 70:30
- 5% fine aluminium powder
- 20 25% CsNO_3
- 25% NH_4Cl
- 10% butadiene

Example 8

- 43.7% red phosphorus
- 25 33.00% CsNO_3
- 6.00% amorphous boron
- 4.75% titanium powder smaller than 100 μm .
- 12.50% polybutadiene

Example 9

- 30 43.75% red phosphorus
- 33.00% CsNO_3
- 6.00% amorphous boron
- 4.75% zirconium/nickel alloy 70:30
- 12.50% Macroplast B 202 (butadiene in solvent manufactured by the firm Henkel, Düsseldorf, FRG).

Patent Claims

1. Pyrotechnical smoke compositions which produce impenetrable smoke in the visible and infra-red range based on halogen donors, as well as metal powders
5 and/or oxides or on the basis of red phosphorus, which contain additional alkali metal salts, characterised in that caesium compounds are additionally admixed with the smoke compositions which are dispersed in the case of combustion and absorb radiations in the infra-red
10 range.
2. Pyrotechnical smoke compositions according to claim 1, characterised in that the content of caesium compounds amounts to 5 - 50%.
3. Pyrotechnical smoke compositions according to
15 claim 2, characterised in that the content of caesium compounds amounts to 5 - 25%.
4. Pyrotechnical smoke compositions according to one of claims 1 - 3, characterised in that caesium chloride, caesium bromide, caesium nitrate, caesium oxide is
20 contained as caesium compound.
5. Pyrotechnical smoke compositions according to claim 1 - 4, characterised in that the caesium compound is admixed with a hexachloroethane composition with silicon and aluminium as metal powder.
- 25 6. Pyrotechnical smoke compositions according to claim 5, containing
50 - 70 wt.% hexachloroethane
20 - 40 wt.% silicon and/or aluminium powder, as well as
5 - 20 wt.% caesium compound.
- 30 7. Pyrotechnical smoke compositions according to claim 1 - 4, characterised in that the caesium compound is admixed with a red phosphorus-containing smoke composition.



8. Pyrotechnical smoke compositions according to claim 7, characterised by a content of zirconium/nickel alloy, preferably in an alloying ratio of 70/30.
9. Pyrotechnical smoke compositions according to claim 8, characterised by an additional content of amorphous boron.
10. Pyrotechnical smoke compositions according to claim 8 and 9, characterised by the following mixture ratio
- | | | |
|----|------------------|----------|
| 10 | red phosphorus | 30 - 50% |
| | zirconium/nickel | 3 - 15% |
| | boron | 5 - 20% |
| | caesium compound | 5 - 25% |
- and possibly aluminium powder in amounts of 3% to 20%.
11. Pyrotechnical smoke compositions according to claim 8 to 10, characterised by additions of ammonium chloride in amounts of 5% to 25%.

