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(54) **Green moulding sands containing fatty acids and trigycerides.**

(57) The invention provides for the use of a material composed of fatty acids and triglycerides of fatty acids of a medium-high degree of insaturation wherein the content of fatty acids is no less than 40%, in order to improve the compositions of green moulding sands used in the foundry. In particular the use of said material in a quantity not less than 0.2% improves the flowability and the plasticity of the sands, and if used in quantities not less than 1%, it becomes a supplier of lustrous carbon with limited production of pollutive substances and free of 3-4 benzo-a-pyrene.

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The present invention relates to the field of foundry and in particular to improvements in the composition of green moulding sands. More precisely the invention relates to the use in said compositions of a lustrous carbon supply material of low pollutive capacity, able to increase the flowability and the plasticity of said sands.

As known, in the foundry techniques for the manufacture of moulds for castings of iron; non ferrous alloys and steels, green moulding sands are used consisting principally of a refractory framework, which is generally siliceous sand, agglomerated with a clay functioninig as a binder. Bentonite can be used successfully as a clay binder. These sands also contain water and, depending on the destination of the mould, particular additives such as carbon additives in the manufacture of iron castings and non ferrous alloys. As known, the presence of the carbon additive allows for a better surface finishing and assists the casting cleaning. As a carbon additive, for a long time the so-called mineral black that is coal was used in powder (100-200 mesh) or in grains (50-150 mesh) obtained from the grinding of the low-grade anthracite. The properties useful for the casting of this additive are derived from an active fraction which is produced from the additive at high temperatures. Said fraction, called "lustrous carbon" is an allotropic state of carbon, optically isotropic, having a microcrystalline structure halfway between those of the amorphous carbon and graphite, essentially bidimensional and obtained on ample surfaces specific from pyrolisis of heavy hydrocarbons emitted from the carbon material during contact with the melted metal. A mineral black having a content of between 30 and 35% volatile substances has a yield of lustrous carbon generally not greater than 10% of its own weight and normally comprised between 6 and 8%. Chemical and physical properties; as well as methods of analysis of the lustrous carbon are broadly described in V.I.Bindermagel, A.Kolors, K.Orths: Procedure for the analysis of the additives to materials for moulds, Giesserei Vol.51,12 Nov., pages 729-730 (1964).

As a carbon additive, in place of the above-mentioned mineral black, substances of synthetic origin can be used (for example polypropylene, cumarone resins, polystyrene, glycerophthalic, resins, gilsonite and pitchy substances, phenolic and hydrocarbonic resins, etc.) which during the fusion process are able to develop lustrous carbon in quantities even greater than 50% of their own weight, and therefore about 10 times greater than that developed from the traditional mineral black. For this reason said substitutive substances for mineral black can be used in proportionately smaller quantities.

All the minerals used in substitution for the mineral black are of organic and in particular aromatic nature, with low or no oxygen content, and a high carbon/hydrogen ratio, in order to resemble as much as possible to coal. However, even if in different amounts, they are materials which, for the effect of heat during fusion at about 1000°C, decompose depositing finely broken down carbon on the surface of depositing finely broken down carbon on the surface of the casting and on the surrounding grains of sands. Along with the lustrous carbon, due to the isomerization caused by the high temperature and in the absence of oxygen, polycyclic and non polycyclic aromatic hydrocarbons and 3-4-benzo-a-pyrene are also formed (the latter being particularly deleterious), developing with the gas during fusion, and polluting often dangerously the air of the work environment.

Naturally these pollutive substances develop also when mineral black is used as the carbon additive. However, in this case given an equal amount of lustrous carbon produced, the pollutive load is considerably higher.

Materials of carbonic nature have also been identified, such as aliphatic oil resins, polyethylenes, and paraffins, which assure an almost satisfactory formation of lustrous carbon, though less than that of the other above-described known materials suitable for the same object, but with a substantially lower production of the above mentioned pollutants. The problem of eliminating the formation of said pollutants almost completely remains unresolved, but continues to be of great interest in foundry as a result of the proven danger of said substances to human health.

Besides the problem of pollution of the work environment, the problem of workability of green moulding sands is also of great interest in casting. In fact the moulding sands are continuosly recycled, reintegrated and regenerated with a quantity of components sufficient to keep its characteristics substantially constant over time. Furthermore, for economic reasons, sand which has already been used for making the cores, but which is generally adequately pure after the disintegration of the organic binder as a result of the heat during fusion, is often reutilized for the moulding sands. This practice can be used especially in the case of series castings, such as radiators and boilers. Precisely in these castings, however, large grain sands of type 3 or 4 with a fineness index of 35-40 are used for the cores in order to facilitate the gas release during fusion, whereas, particularly in the radiators for which a better surface finishing is required, fine sands tend to be used for the moulding. The introduction of the core sand therefore creates some problems because of its increased tendency towards superficial penetration of the metal, and creating a rougher surface of the castings. More generally the recycled sands are not homogenous and have clots which are caught in the filter along with other gross impurities. It should be noted that the clots are particularly bentonite-rich and therefore their elimination from the cycle implies an impoverishment of the moulding sands, a binder make-up being consequently necessary.

The problem of improving the workability of the sand is of great interest in the field both for reducing the mulling and moulding times as well as for obtaining higher quality castings. To that end, in European patent application no. 0 218 552 in the name of the same Applicant, an additive of organic nature and of a stabilized carbohydrate base was proposed to improve the flowability of the green moulding sands developing the binding properties of the bentonite and reducing considerably the demand of water. The additive according to this patent was essentially a plasticizer of the bentonite.

The object of the present invention is to improve the composition of green moulding sands with the purpose of both further reducing, and possibly eliminating, from the work environment the pollutants most harmful to health which develop from the lustrous carbon supply materials until now utilized, as well as improving the flowability and the plasticity of the green moulding sands.

Another object of the present invention is to provide a method for manufacturing moulds in casting the execution of which results in a reduction of the pollutive load of the work environment and better workability of the green moulding sands.

A further object of the present invention is to provide a material, utilizable as an additive for the green moulding sands, which is able on one hand to provide sufficient quantities of lustrous carbon while causing fewer pollution problems than the additives currently used for the same object, and on the other to contribute to improving the flowability, plasticity, and therefore workability, of the green moulding sands.

The accomplishment of these objects has been possible thanks to the present invention according to which certain carbon materials, consisting of a mixture of fatty acids and glycerides of fatty acids at a medium-high degree of insaturation, wherein the percentage of free fatty acids is at least 40% and preferably not more than 90%, are proposed as additives for the green moulding sands both as suppliers of lustrous carbon of a low pollutive load as well as for their suitability for improving the workability of the sands themselves.

The term "medium-high degree of insaturation" is intended as an average number of double bonds comprised between 2 and 3 for each molecule of free fatty acid.

The average indicative composition of the materials according to the present invention is:

triglycerides	15-25% by weight
free fatty acids	50-65% " ""
other esters of fatty acids	10-15% " ""
unsaponifiable substances	3-5% " ""

It has been found that the material according to the present invention is able to develop a quantity of lustrous carbon equal to 35-40% of its own weight and, contemporaneously, that during the fusion process in the gasses of thermic decomposition, emitted in the work environment, 3-4 benzo-a-pyrene is not detected, and the mono- and polynuclear aromatic hydrocarbons are present in much smaller quantities than found with the currently used carbon additives. This is probably due to the presence of insaturations in the aliphatic chain and of other types of bonds such as etereal and estereal which prevent the formation of condensed and non condensed aromatic nuclei.

Furthermore it has been found that a low content of material according to the present invention is sufficient in the green moulding sand to make it considerably more fluid. Said content is on the order of 0.5-1% of the weight of the sand and in any case not less than 0.2% by weight. Used in an average quantity of 0.5% by weight, with periodic additions during the cycle of moulding sands of at least 0.01% and, in particular, of 0.02-0.03% to make-up the quantity destroyed during fusion, the additive according to the present invention confers the following characteristics to the green sands:

a - increases the plasticity of the sand, for which reason moulds of higher density and therefore higher specific resistance are obtained thus allowing the production of complex castings;

b - improves the flowability and the shake-up factor, and eliminates the formation of clots after fusion;

c - reduces the penetration of the metal, even if the sand contains larger grains, originating from the cores, as a result of the increased plasticity;

d - allows operation with a smaller quantity of water.

When the material according to the present invention is used in quantities greater than 1% of the overall weight of the sand, it acts as a provider of lustrous carbon, besides naturally maintaining its above-mentioned effect on the workability of the sands. The quantity preferred for this function is comprised between 1.5 and 3.5%. As a comparison it should be remembered that using mineral black of a traditional type or one of its substitutes, for instance a petrolic resin, the minimum percentage to be added to the sands is normally above 5%

and 1% respectively.

Depending on the origin of the material according to the present invention, the percentages of free fatty acids in it are:

oleic acid	25-65%
stearic acid	0-10%
palmitic acid	10-20%
linolic-linolenic acid	10-50%

A particularly preferred material for the objects of the present invention has a percentage content of free fatty acids as shown in the following table 1:

TABLE 1

oleic acid	30%
palmitic acid	10%
linolic and linolenic acid	30%
total content of fatty acids	70%
Its other typical properties are the following:	
freezing point	9-10°C
boiling point	240°C
apparent specific weight at 20°C	0.900
density at 70°C	0.870
flash point	260°C
autoignition temperature	300°C
acidity number	50-60
iodine number	90-120
Elementary Analysis	
carbon about	80%
hydrogen about	10%
nitrogen	1%
sulphur	absent
oxygen about	10%

In table 2 which follows, the analyses of the products of decomposition at 1000°C developed from the material according to the present invention (column A), from an aromatic petrolic resin (column B) and from a normal mineral black (column C) are set forth for the purpose of comparison.

TABLE 2

AROMATICS, POLICYCLICS in mg/Kg			
	A	B	C
Naphthalene	3.975	21.600	9.100
Acenaphthalene	530	2.100	1.500
Acenaphthene	230	1.200	1.050
Fluorene	235	450	900
Anthracene+Phenanthrene	1.100	2.700	5.333
Fluoranthene	700	1.350	187
Pyrene	575	1.100	205
3-4 benzo-a-pyrene	nd	900	134
Benzofluorene	nd	1.500	250
Benzoanthracene	nd	13.500	278
TOTAL	7.345	46.500	18.937
Lustrous Carbon %	40	60	7
Pollution factor	183	775	2.705

From the examination of the data set forth in the previous table it can first of all be observed that the material according to the invention does not cause the production of 3-4 benzo-a-pyrene. This fact alone makes preferable without a doubt the use of this material as a supplier of lustrous carbon. In fact, in accordance with the laws presently in force, while the total threshold value for the various polynuclear hydrocarbons is 0.2 mg/kg, the same value for 3-4 benzo-a-pyrene is zero; in other words this pollutant should not be present.

Furthermore it is observed that, if the pollution factor resulting from the polycyclic hydrocarbons is expressed as a function of the released lustrous carbon, the quantity of which in practice determines the quantity of carbon material used, it results that material according to the present invention is more than seven times less pollutive than the aromatic petrolic resins and almost fourteen times less pollutive than the mineral black.

In the procedure followed for the preparation of the green moulding sands, the material according to the present invention, which is in a liquid form, can be added to the other components of the sand (siliceous sand, binder, water and additives) during the mulling step in the percentages defined above, or it can be added in the form of a premix with the binder, with or without other additives, further simplifying the operations of preparation of the moulding mixture. The binder premixed with the material according to the invention can be made available in two different concentrations, respectively with a percentage of 40-50% and 5-10% by weight of the above-mentioned material, according to whether it is to be used as a supplier of lustrous carbon or only to improve the workability of the sand.

In both cases the material according to the present invention can be supplied to the foundries in a liquid form, in drums or in bulk of 20 t, or, in a solid form, previously adsorbed in the above said proportions with the binder, for example bentonite, which can also contain other additives and conditioners of common use according to the needs of the foundries utilizing them.

To make more apparent the modalities of use of the additive according to the present invention, the following practical, non limitative examples are given.

EXAMPLE 1

A moulding sand containing the material described in the present invention, to be utilized in foundries of cast iron or non ferrous alloys such as bronze, brass and aluminum, for castings of medium thickness, can have the following composition:

Siliceous sand	100 parts by weight
Sodium Bentonite	6-8 "" " ""
L.C. supplying material	1.2-1.5 " " ""
Humidity	3-3.5 " " ""

As a lustrous carbon supplying material according to the invention a mixture of fatty acids and glycerides of fatty acids is used, obtained as a by-product of industrial processing and having a composition and chemophysical characteristics equal to those set forth in the previous tables. This moulding sand, once in cycle, can be made-up with 1.1% of new sand, if the castings have few cores and their sand does not go in the moulding sand, with 0.3-0.4% bentonite in relation to the thickness of the castings produced and with 0.05-0.1% lustrous carbon supplying material. If the lustrous carbon supplying material is provided to the foundry in the form of a premix with bentonite, containing 40-50% of the former and 50-60% of the latter, the composition of the moulding sand, for the same type of iron castings will be:

Siliceous sand	100 parts by weight
Sodium Bentonite	4.8-6.5 " " ""
50% Premix	2.4-3 " " ""
Humidity	3.0-3.5 " " ""

To make-up the sand, the same quantity of new sand as the previous case, the same quantity of bentonite minus the quantity contained in the premix and twice the quantity of premix as in the preceding case are used since half of the premix is composed of bentonite.

EXAMPLE 2

For larger castings, whose nature implies high and wide vertical walls, the composition can be:

Siliceous sand	100 parts by weight
Sodium Bentonite	8-10 "" " ""
L.C.supplying material	1.5-1.8 " " ""
Humidity	3.5-4 "" " ""

The make-up quantities, considering the weight of the castings, can be increased slightly, in order to maintain the same technological properties of the sand. That is, bentonite can reach 0.4-0.45, and the lustrous carbon supplying material can be added in an amount of 0.1%; if however a premix of lustrous carbon supplying material and bentonite is used, the above additions are proportionately changed.

EXAMPLE 3

To make more apparent the advantages arising from the use of the material according to the present invention to improve the workability of the green moulding sands, tests were carried out on moulding sands of the above mentioned material without such a material (A) and with such a material (B). According to the usuale techniques, samples were prepared with the following composition:

	SAMPLES	
	A	B
55-60 I.F Sand	3000 g	3000 g
A.G.Bentonite	150 g	150 g
Water	120 g	100 g
L.C.supplying material	----	30 g

The weight of the samples (samples of cylindrical form with diameter 50 mm and height 50 mm), the moulding pressure being equal, was found to be considerably higher in case B. In figure 1, diagrams a) and b), respectively show the curve of the weight of the samples A and B as a function of the humidity content. As can be noted, for example, with a humidity content of 3%, sample B weighs about 161 g, whereas sample A weighs 152 g. This means that the moulding sand containing the additive according to the invention is able of being more compacted because it is more plastic.

For the same samples A and B, the Shatter index as a function of the humidity was measured. As shown in figure 2, diagrams a) and b), the Shatter index is greater for sample B containing the material according to the invention (figure 2%). For instance, samples containing 3% humidity have a Shatter index equal to 65 and 83 respectively. The Shatter index is a parameter which is directly proportional to the mouldability of the sand.

The material according to the present invention can be made by mixing mostly unsaturated fatty acids and triglycerides of the same fatty acids in a proportion to reach a minimum content of fatty acids of no less than 40%, or by-products of industrial processing containing said substances and suitable for use in casting can be used.

Claims

1. Composition for green molding sands comprising at least siliceus sand, a clayey binder and water, characterized in that it further comprises a material substantially comprising fatty acids and glycerides of fatty acids with a medium-high degree of insaturation, the percentage of free fatty acids in said material being comprised between 40 and 90% by weight.

2. Composition according to claim 1, wherein said material has the following average composition by weight:

Triglycerides	15-25%
Free fatty acids	50-65%
Other esters of fatty acids	10-15%
Unsaponifiable substances	3-5%

3. Composition according to claims 1 and 2, wherein the percentages of the various free fatty acids present in said material are:

Oleic acid	25-65%
Stearic acid	0-10%
Palmitic acid	10-20%
Lonolic-Linolenic acid	10-50%

4. Composition according to claims 1 to 3, wherein said material is used as a supplier of lustrous carbon and is present in an amount of no less than 1% of the total weight of the sand.

5. Composition according to claim 4, wherein the amount of said material is comprised between 1.5-3.5% by weight.

6. Composition according to claims 1 to 3, wherein said material is used to improve the workability of said sand and is present in an amount of no less than 0.2% by weight.

7. Composition according to claim 6, wherein the quantity of said material is comprised between 0.5 and 1% by weight.

8. Method for the manufacture of moulds in the foundry characterized by the fact that it comprises the following steps:
   - providing a green moulding sand formed by at least siliceous sand, clayey binder, additives and water;
   - adding an amount of material substantially comprising fatty acids and glycerides of fatty acids of a medium-high degree of insaturation in which the percentage of free fatty acids is at least 40% by weight, said amount being sufficient to confer flowability and plasticity to said sand or to provide the necessary quantity of lustrous carbon;
   - mixing said components; and
   - shaping said sand into the desired form.

9. Method according to claim 8, wherein said material, if used as a supplier of lustrous carbon, is added in a quantity not lower than 1% of the total weight of the sand.

10. Method according to claim 9, wherein the quantity of said lustrous carbon supplying material added is preferably comprised between 1.5 and 3.5 of the total weight of the sand.

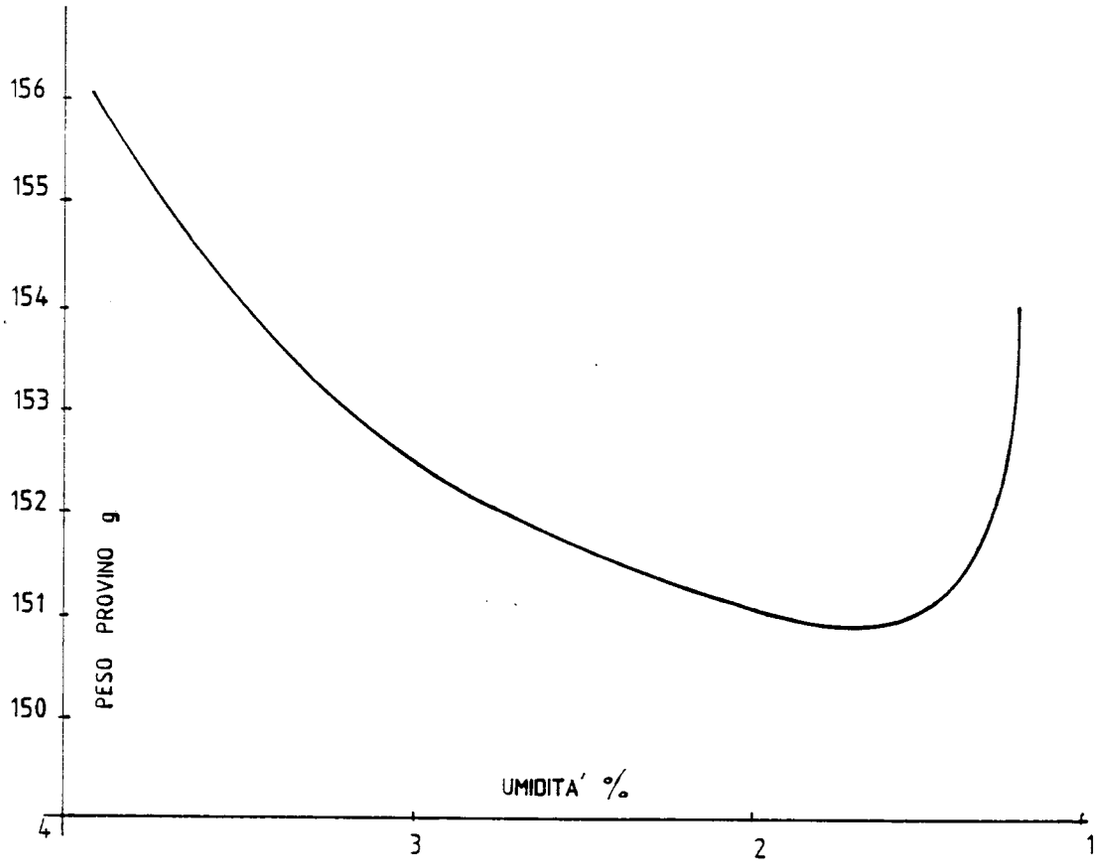
11. Method according to claim 8, wherein said material, if used to improve the flowability and plasticity of the sand, is added to said sand in a percentage not lower than 0.2% by weight.

12. Method according to claim 11, wherein said material is added in a percentage by weight comprised between 0.5 and 1% by weight.

13. Method according to claims 11 and 12, wherein said moulding sand comprising said lustrous carbon supplying material is recycled, and at each cycle a make-up quantity of said material of at least 0.02% is added.

14. Method according to claims 6 to 13, wherein said material is premixed with the binder in a form with or without other additives.

15. Material for improving the workability of green moulding sands and for providing them with an effective amount of lustrous carbon substantially as claimed in any one of claims 1 to 7.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4
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Fig. 1a

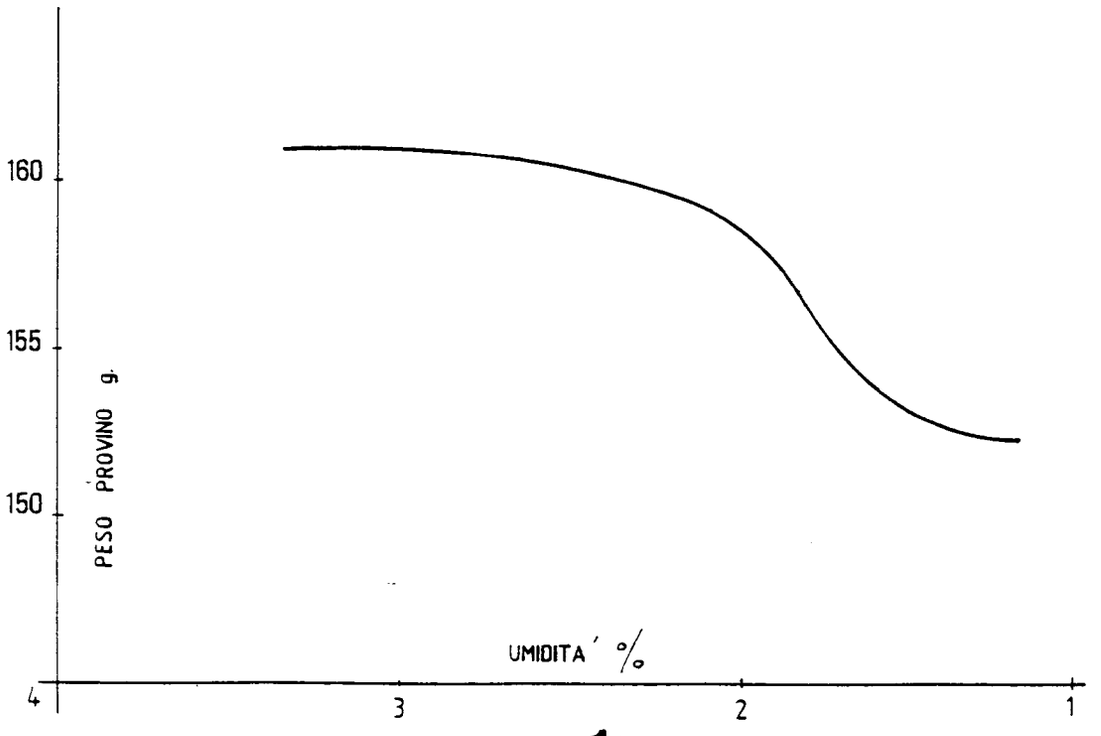
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Fig. 1b

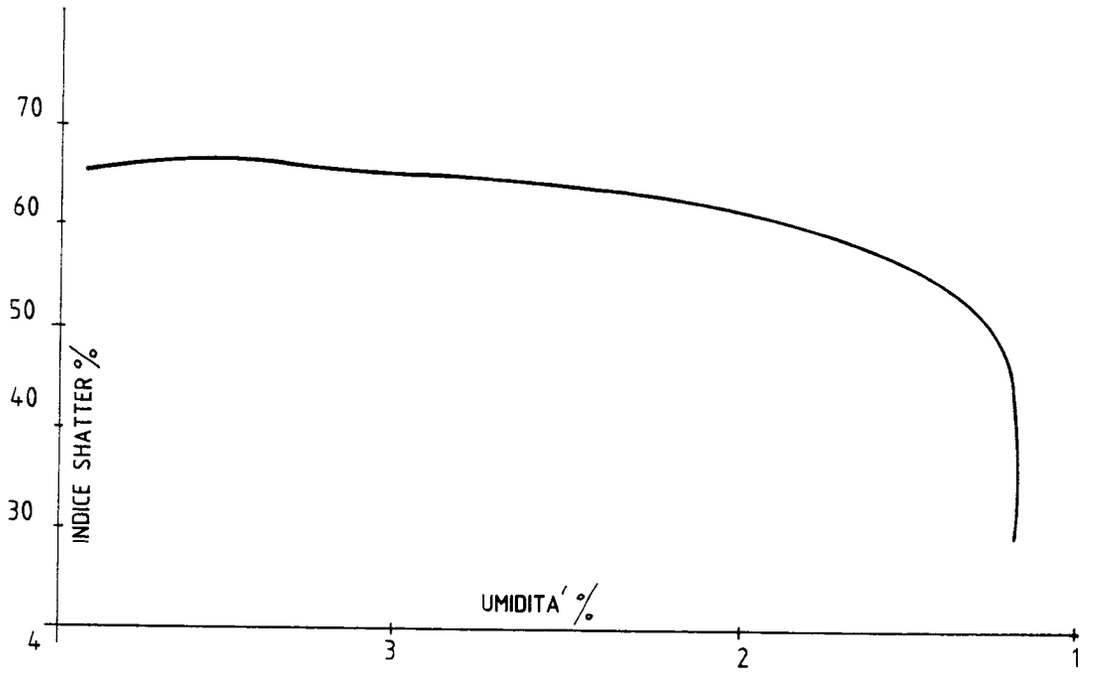
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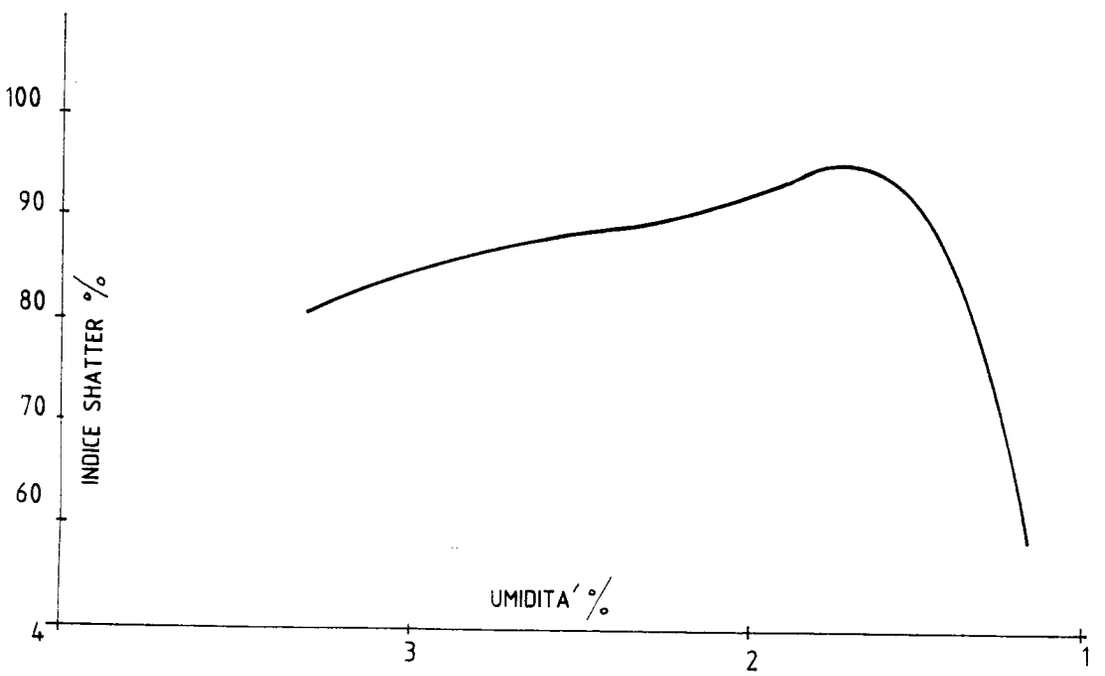
Fig. 2 a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INDICE SHATTER %
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UMIDITA' %

Fig. 2 b

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 83 0679

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-2 272 483 (SHEELY) 10 February 1942 * whole document *	1,2,4, 6-9,11, 12,15	B22C1/02 B22C1/24
X	CH-A-273 466 (OEL- UND CHEMIE-WERK AG) 1 May 1951 * claims *	1	
A	DATABASE WPI Week 7636, Derwent Publications Ltd., London, GB; AN 76-68187X [36] & SU-A-490 553 (BARYSHEVSKII) 13 February 1976 * abstract *	1,4,5, 8-10,15	
A	DATABASE WPIL Week 8208, Derwent Publications Ltd., London, GB; AN 82-15260E [08] & SU-A-827 241 (ISAEVA) 22 May 1981 * abstract *	1,4,5, 8-10,15	TECHNICAL FIELDS SEARCHED (Int. Cl.5) B22C
A	DATABASE WPIL Week 9118, Derwent Publications Ltd., London, GB; AN 91-130762 [18] & SU-A-1 569 331 (DAGESTAN POLY) 7 June 1990 * abstract *	1,2,6-8, 11-12,15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31 MARCH 1993	RIBA VILANOVA M.

CATEGORY OF CITED DOCUMENTS

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