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(54) Title: PROCESS FOR THE PRODUCTION OF POLYMERIC SULPHUR

(57) Abstract: The patent covers a new and original process for the production of polymeric sulphur. The process involves a crosslinking reaction of molten sulfur with opportune crosslinking agents added with the twofold scope of increasing the yields and to stabilize the polymeric allotrope of sulphur which is formed at high temperature. Furthermore, the new process involves the adoption of a new safer solvent for the purification of the polymeric sulphur and the elimination of the dangerous and toxic CS₂.



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PROCESS FOR THE PRODUCTION OF POLYMERIC SULPHUR

Summary

The patent covers a new and original process for the production of polymeric sulphur. The process involves a crosslinking reaction of molten sulfur with opportune crosslinking agents added with the twofold scope of increasing the yields and to stabilize the polymeric allotrope of sulphur which is formed at high temperature. Furthermore, the new process involves the adoption of a new safer solvent for the purification of the polymeric sulphur and the elimination of the dangerous and toxic CS₂.

Introduction

10 The polymeric sulphur is a fundamental raw material for the rubber industry. In fact it is used as curing agent or, which is the same, as chemical agent which is able to form crosslinks between adjacent diene polymer chains during the vulcanization process, giving a definitive and permanent elasticity and form to any rubber article. The polymeric sulphur is known to the experts of the art also as "insoluble sulphur" because, just for its
15 macromolecular chemical structure, is completely insoluble in any organic solvent, including carbon disulfide which is the best solvent for common sulphur (cyclooctasulphur). The polymeric sulphur can be distinguished from common sulphur or rhombic sulphur just for its high molecular weight and chemical structure, being in fact made by long chains of sulphur atoms arranged according to defined supramolecular
20 structures (see for more details: F. Cataldo, Die Angewandte Makromolekulare Chemie vol. 249, p.137-149, 1997). The molecular weight of polymeric sulphur is of the order of 10⁶ Dalton, as determined by ESR measurements. In contrast, common sulphur is a molecular solid whose molecules are made by 8 sulphur atoms arranged in eight-member rings, each of which has a molecular weight of 256 Dalton. In fact, just because of its
25 molecular structure, the common sulphur is called also cyclooctasulphur. The molecules of cyclooctasulphur in the solid state form rhombic crystals or, under special conditions, monoclinic crystals. The cyclooctasulphur crystals are soluble in the common organic solvents thanks to the low molecular weight of the molecules composing these crystals.

Certainly, the polymeric sulphur represents a technological alternative to the common
30 sulphur and it is employed as replacement of the latter under well defined circumstances, for instance when sulphur blooming phenomena represent a major problem in the

manufacture of rubber compounds (see more details on this aspect on: F.Cataldo, 1997, cit.).

The process commonly used in the current art to produce polymeric sulphur is energetically demanding and not particularly attractive from the technical point of view in terms of safety and environmental impact. In fact, the process currently adopted industrially, involves the high temperature sublimation of sulphur, possibly with overheating of the vapours up to 675°C (note how it is energetically demanding this process), see S. Alvin, U.S. Pat. 2,513,524 of 04-07-1950 and R.E. Morningstar, U.S. Pat. 2,667,406 of 26-01-1954, sometime in presence of H₂S (cfr. S. Kyung, U.S. Pat. 4,359,452 of 16-11-1982) followed by a quenching step of the vapour in an opportune cooling medium which normally consists of liquid CS₂ (cfr. S. Kyung, cit.). Therefore, the current art involves demanding technical and engineering problems but also enormous safety problems being well known both the toxicity and the extremely high flammability of CS₂.

Some year ago, we proposed a new and revolutionary process (cfr. F.Cataldo, PCT/EP00/06013 of 28-06-2000 and WO0200549 of 03-01-2002) for the production of polymeric sulphur, starting from the hydrolysis of chlorosulphanes, a series of sulphur chlorides having the general formula S_xCl₂, in a reaction which leads exclusively to polymeric sulphur avoiding in this way the need to extract the product with the dangerous CS₂ to separate the soluble sulphur component from the polymeric sulphur.

With the present patent dealing with a process of melting and crosslinking sulphur followed by the purification of the polymeric sulphur with diiodomethane (CH₂I₂) , we would like now to cover an alternative process to both our previous invention mentioned above and the current industrial art consisting in the rapid quenching of the superheated sulphur vapours followed by an extraction step with CS₂. More in detail, with the present patent, we desire to cover a process involving sulphur melting at temperature comprised between 150° and 444°C in presence of one ore more sulphur additives acting as crosslinking agents followed by a rapid cooling or quenching of the molten sulphur in an opportune medium, preferably cold water, cold hydrogen peroxide, a chilled organic solvent or even a cryogenic medium such as liquid air or liquid nitrogen. Furthermore, the present patent covers a process for the purification of the polymeric sulphur produced, by an extraction step made with diiodomethane (CH₂I₂) in place of the currently used CS₂. In contrast with CS₂, diiodomethane is not flammable and does not present the toxicity and

health concerns of CS₂. Therefore, it can be affirmed that the newly proposed process described in the present patent represents also a real breakthrough in the specific art for a series of advantages ranging from the simplicity, the energy saving, the health and environmental impact.

5 The process of sulphur melting to temperatures where the partial sulphur polymerization occurs because of the ring-chain equilibrium, followed by quenching, is a well known process. In fact it is known that the sulphur brought at high temperatures and, to be precise, at temperatures above 170°C consists of an equilibrium of at least two species: cyclooctasulphur and chain-sulphur having variable length and hence molecular weight
10 (cfr. F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley- Intersciences, p.406-409, 1962). If the melt is quenched, it gives a mixture of polymeric sulphur and cyclooctasulphur in the approximate proportion of 25% and 75% respectively. The cyclooctasulphur present in the mixture can be removed through an extraction process using for instance CS₂ as solvent. However, the insoluble sulphur prepared in this way is in
15 a metastable form and in few hours or days it is fully reverted to cyclooctasulphur. The process involving the passage from polymeric sulphur to cyclooctasulphur is known as "reversion". Therefore, the simple sulphur melting process in the form just described above is not suitable for any industrial application both for the very low stability of the polymeric sulphur produced with such a process and for the low yields in polymeric sulphur offered
20 by the mentioned process: just about 25%.

It has now been found, and it is the object of the present invention, that heating of sulphur together with opportune sulphur crosslinking agents such as the elements of the 5th group of the Periodic Table: P, As, Sb, Bi in their elemental state or under the form of derivatives like for instance their sulfides, selenides, tellurides or halides, causes both a neat increase
25 in the yields of insoluble sulphur but also a neat improvement in the reversion resistance of the produced sulphur.

In its preferred form of actuation of the present invention, the preference as crosslinking agent has been given to elemental phosphorous in its red modification in any stoichiometric ratio with sulphur but preferably in S/P ratio between 40 and ∞. Elemental
30 phosphorus can be replaced by its derivatives under the form of all class of phosphorus sulphides, phosphorus selenides and phosphorus tellurides in general, with preference for tetraphosphorus decasulphide (P₄S₁₀) or tetraphosphorus trisulphide (P₄S₃) as crosslinking

agents and yield enhancers in the production of insoluble sulphur. More in detail, we have observed that elemental phosphorus and certain phosphorous sulphides or halides like phosphorus pentachloride show a very clear activity both in the promotion of the formation of polymeric sulphur and in the stabilization of its polymeric form. In this context, it is worth mentioning that we have also found, and therefore it is part of the present patent, that also the combination of elemental phosphorus or phosphorus sulphides with elemental halogens such as chlorine, bromine or iodine or halogen-bearing molecules such as disulphur dichloride (S_2Cl_2) or sulphur dichloride (SCl_2) is a very effective combination for reaching both an high yield in insoluble sulphur and an high reversion stability. The typical preferred stoichiometric ratios among the mentioned elements are reported in the examples but are not in any way limiting.

Therefore, the object of the present invention is a process which involves the melting of sulphur in presence of an adequate crosslinking agent or crosslinking agents mix, as detailed above, at temperatures comprised between $150^{\circ}C$ and $444^{\circ}C$, for times ranging from 1 hour to several hours. In order to ensure an high yield in polymeric sulphur, the melt must be rapidly cooled in an opportune quenching medium consisting of cold water, cold hydrogen peroxide, a chilled organic solvent, preferably diiodomethane, or even a cryogenic medium like liquid air or liquid hydrogen. The melt must be poured in a quenching medium in such a way to ensure the maximum exchange of heat in the shortest possible time. The best way to do this is to pour the melt into the quenching medium under the form of thin threads. The purification of the polymeric sulphur formed in the process involves the extraction of the cyclooctasulphur from the product. This may be performed during the quenching step or after a "maturation" period. As discussed previously, the present invention requires the use of diiodomethane as extraction and purification solvent rather than carbon disulfide with the advantage of much lower toxicity and no flammability. In this aspect the invention represents a big step ahead in the process safety, an innovation which is part of the invention itself. The following examples illustrate the invention in its preferred form of actuation. It is obvious that changes and variations can be easily introduced by experts in the art without exiting from the field protected by the present patent.

EXAMPLES 1-20

A typical procedure is now described. All the other examples are reported in Table 1. All chemicals used in this study were obtained from Sigma-Adrich srl, Milan, Italy.

- A round bottomed spherical flask equipped with a mechanical stirrer and a vent valve, is
- 5 charged with 1000g of powdered sulphur together with an adequate amount of a crosslinking agent needed to respect the stoichiometric ratio between sulphur and the additive (see Table 1). Just as an example, if we look at example 6 of Table 1, for 1000 g of sulphur, 13 g of tetraphosphorus decasulphide (P_4S_{10}) are used in the melt. The flask once charged with the components, is heated in an oil bath to the sulphur melting point.
- 10 Then the mixture is stirred slowly to homogenize the components and heated up to about 190°-220°C. At this point the stirring speed is increased to the maximum value and the system is kept under the described conditions for 1 hour. At the beginning of the second hour the temperature is brought at 240°-280°C and at the end of the second hour the mass is poured as a thin thread into a large cup filled with cold water.
- 15 The sulphur threads solidify into a solid elastic coil. The sulphur is left to crystallize at room temperature for at least one day. Then the sulphur is crushed in a mortar and grinded in an opportune mill to powder form. The yields have been always quantitative in all examples.

- The powdered sulphur has then been extracted with CH_2I_2 (methylene iodide or
- 20 diiodomethane). Through the extraction with CH_2I_2 it was possible to separate the soluble sulphur (cyclooctasulfur) from the polymeric and insoluble sulphur. After the extraction the polymeric sulphur was rinsed with dichloromethane (CH_2Cl_2) and dried in air. The yield in insoluble sulphur has been determined gravimetrically (see Table 1 for a summary of the results). The solvent extraction causes sometimes the agglomeration and clumping
- 25 of the particles of insoluble sulphur which need to be grinded again after the extraction process.

- As can be deduced from Table 1, the simple melting of pure sulphur without any additive permits the preparation of polymeric sulphur with 26% yield only. All the additives or crosslinking agents tested in Table 1 are instead able to increase the yield in polymeric
- 30 sulphur in a drastic way. Obviously, the effectiveness of each additive depends both from its chemical nature and from its stoichiometric ratio with sulphur. From Table 1 it can be deduced that the phosphorus sulphides alone or in combination with halogens and sulphur

halides have given the best results. After 6 months and after 1 year from the preparation of the samples reported in Table 1, the level of insoluble sulphur in the samples has been re-checked in some cases. In the sample prepared according to example 1 (without any additive) the level of insoluble sulphur was found 0% already after 6 months from the preparation, in all other samples it has been observed a reduction of the level of polymeric sulphur of the order of magnitude of 3% per year or less, hence confirming the stabilizing effect of all substances tested as crosslinking agents and thereof mixtures.

TABLE 1

EXAMPLES	CROSSLINKING ADDITIVE(S)	ATOMIC RATIO	YIELD % POLYMERIC SULPHUR
1	NONE (Blank)	S	26,0
2	P ₄ S ₁₀	S ₄₄ P	61,9
3	P ₄ S ₁₀	S ₈₈ P	40,0
4	P ₄ S ₁₀	S ₁₁₉ P	43,7
5	P ₄ S ₁₀	S ₁₂₆ P	49,8
6	P ₄ S ₁₀	S ₂₇₅ P	37,6
7	P ₄ S ₁₀ + S ₂ Cl ₂	S ₄₅ ClP	77,0
8	P ₄ S ₁₀ + S ₂ Cl ₂	S ₅₄ Cl ₄ P	49,5
9	P ₄ S ₁₀ + S ₂ Cl ₂	S ₆₀ ClP	89,8
10	P ₄ S ₁₀ + S ₂ Cl ₂	S ₂₁₂ Cl ₁₅ P	47,6
11	P ₄ S ₃	S ₁₄ P	89,5
12	P ₄ S ₃	S ₇₄ P	67,0
13	P ₄ S ₃	S ₃₀₂ P	50,0
14	P ₄ S ₃	S ₆₂₄ P	43,3
15	PCl ₅	S ₄₀ PCl ₅	44,4
16	PCl ₅	S ₁₃₆ PCl ₅	32,5
17	I ₂	S ₂₀₈₃ I	38,5
18	I ₂ + P ₄ S ₁₀	S ₁₄₆₁ PI ₇	46,6
19	I ₂ + P ₄ S ₁₀	S ₈₈ PI _{0,009}	56,1
20	Cl ₂	S ₁₅₀ Cl	39,4
21	Red Phosphorus Phosphorous+	S ₅₅ P	67,3
22	S ₂ Cl ₂	S ₁₉₀ Cl ₁₂ P	55,8
23	Phosphorous+ I ₂	S ₁₂₂ PI _{0.03}	50,9
24	Phosphorous+ I ₂	S ₂₁₀₀ PI _{0.05}	42,4

Example 1 refers to the "blank" i.e. the reference level of polymeric sulphur reachable without additives. For atomic ratio we intend the ratio between the various elements in the

melt. For instance, with “S₁₄₆₁PI₇” we mean that every 1461 sulphur atoms there is one phosphorus atom and 7 iodine atoms.

CLAIMS

1. A process for the production of polymeric sulphur insoluble in carbon disulphide consisting in melting sulphur in presence of one or more additives which are able to crosslink the chains of polymeric sulphur and/or to stabilize the chain ends and to improve the yields.
2. Process according to claim 1 where the temperature at which is kept the mass of molten sulphur is comprised between 150° and 444°C and preferably above 200° to 444°C.
3. Process according to claims 1 and 2 where the sulphur crosslinking and stabilizing additive is an element or a derivative of the mentioned element selected among the elements of the 5ath group of the Periodic Table of the Elements (N, P, As, Sb, Bi), taken alone or in combination with other elements and hence under the form of a sulphide a selenide, a telluride and an halide.
4. Process according to claim 3 where the element added to the molten sulphur is elemental phosphorus under any allotropic form, but preferably as red phosphorus and in an atomic ratio with sulphur comprised between an S/P = ∞ to an S/P = 1 and preferably from 40 to ∞.
5. Process according to claim 4 where phosphorus instead of being added in elemental form is added under the form of a sulphide, a selenide or a telluride of phosphorus in general and under the form of tetraphosphorus trisulphide (P₄S₃) or tetraphosphorus decasulphide (P₄S₁₀) in particular.
6. Process according to claims 1 and 2 in which the crosslinking and stabilizing additive is an element or a derivative of said element chosen among the elements of the group 6ath of the Periodic Table of the Elements (S, Se, Te) or from the group 7ath of the Periodic Table (F, Cl, Br, I), taken alone, in combination with other elements of the same group, in combination with the elements of the group 7ath if the element belongs to the group 6ath or in combination with other elements outside those of groups 6ath and 7ath.
7. Process according to claims 3 and 6 where the crosslinking element is an elemental halogen like for instance chlorine and/or iodine (Cl₂ and/or I₂), an interhalide like for instance iodine chloride (ICl) and/or a compound containing halogen atoms like for example a chlorosulphane S_xCl₂ with x between 1 and ∞ and/or a phosphorus

halide in general and phosphorus trichloride (PCl_3) or phosphorus pentachloride (PCl_5) in particular.

8. Process according to claims from 1 to 7 included, where instead of using a single crosslinking additive, two or more additives are used simultaneously, like for
5 example the combination of S_2Cl_2 and P_4S_{10} reported in the examples 7,8,9,10 of Table 1 or in the combination between iodine and P_4S_{10} reported in the examples 18 and 19 of Table 1.
9. Process according to claims from 1 to 8 where the mass of molten sulphur with the additive is poured as thin tread in an opportune quenching medium preferably cold
10 and liquid.
10. Process according to claim 9 where the cooling or quenching medium is cold water.
11. Process according to claim 9 where the cooling medium is hydrogen peroxide at any concentration.
12. Process according to claim 9 where the cooling medium is a chilled organic solvent
15 in general and diiodomethane (CH_2I_2) in particular.
13. Process according to claim 9 where the quenching medium is liquid air.
14. Process according to claim 9 where the quenching medium liquid nitrogen.
15. Process according to claims from 1 to 14 where the sulphur cooled and preferably partially crystallized after the melting and quenching steps, is extracted, after
20 grinding, with an opportune solvent which is able to separate the soluble fraction from the insoluble polymeric fraction.
16. Process according to claim 15 where the extraction solvent is a pure halogenated solvent, a mixture of halogenated solvents.
17. Process according to claim 16 where the halogenated solvent is diiodomethane,
25 known also as methylene iodide (CH_2I_2) used pure or in combination with other solvents.
18. Process according to claim 16 where the extraction solvent is tetrachloroethylene ($\text{Cl}_2\text{C}=\text{CCl}_2$) used pure or in combination with other solvents.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B17/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 947 614 A (JULIUS MANTHEY ERNST) 2 August 1960 (1960-08-02) column 5, line 24 - line 26; claims ---	1-3,6,7, 9-18
X	FR 1 120 493 A (RUHRGAS AG) 6 July 1956 (1956-07-06) page 1, left-hand column; claims --- -/--	1-3,6,7, 9-18



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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