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Eljárás térhálósított elasztomer anyag devulkanizálására

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

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(54) **METHOD OF DEVULCANIZING A CROSS-LINKED ELASTOMERIC MATERIAL**

VERFAHREN ZUR ENTVULKANISIERUNG EINES VERNETZTEN ELASTOMEREN MATERIALS
PROCÉDÉ DE DÉVULCANISATION D'UN MATÉRIAU ÉLASTOMÈRE RÉTICULÉ

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(56) References cited:
**WO-A1-2012/007949 CN-A- 1 385 461
US-A- 5 597 851 US-A1- 2011 301 302**

- **MOURI M ET AL: "DE-VULCANISATION CONDITIONS AND MECHANICAL PROPERTIES OF RE-VULCANISED RUBBER FOR EPDM. CONTINUOUS RECLAMATION OF RUBBER BY SHEAR FLOW REACTION CONTROL TECHNOLOGY (PART II)", INTERNATIONAL POLYMER SCIENCE AND TECHNOLOGY, RAPRA TECHNOLOGY, SHREWABURY, GB, vol. 27, no. 1, 1 January 2000 (2000-01-01), pages T23-T28, XP000928158, ISSN: 0307-174X**
- **MOURI M ET AL: "CONTINUOUS DEVULCANISATION BY SHEAR-FLOW STAGE REACTION CONTROL TECHNOLOGY FOR RUBBER RECYCLING PART 4. DEVULCANISATION MECHANISM FOR EPDM", INTERNATIONAL POLYMER SCIENCE AND TECHNOLOGY, RAPRA TECHNOLOGY, SHREWABURY, GB, vol. 27, no. 2, 1 January 2000 (2000-01-01), pages T17-T22, XP000975424, ISSN: 0307-174X**
- **MOURI M ET AL: "CONTINUOUS DEVULCANISATION BY SHEAR FLOW STAGE REACTION CONTROL TECHNOLOGY FOR RUBBER RECYCLING PART 3. STUDY OF THE DEVULCANISATION PROCESS FOR EPDM", INTERNATIONAL POLYMER SCIENCE AND TECHNOLOGY, RAPRA TECHNOLOGY, SHREWABURY, GB, vol. 27, no. 2, 1 January 2000 (2000-01-01), pages T12-T16, XP000975423, ISSN: 0307-174X**

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- **Walter C. Warner: "Chemical Methods of Devulcanizing Thermoset Rubber" In: "Plastics, Rubber, and Paper Recycling", 5 May 1995 (1995-05-05), American Chemical Society, Washington, DC, XP055143568, ISBN: 978-0-84-121540-5 vol. 609, pages 245-253, DOI: 10.1021/bk-1995-0609.ch021, * page 247, paragraph 3 - paragraph 4 ***
- **GOETHALS E J ET AL: "DE-CROSSLINKABLE NETWORKS", MAKROMOLEKULARE CHEMIE, MACROMOLECULAR SYMPOSIA, HUTHIG UND WEPF VERLAG. BASEL, CH, vol. 48 / 49, 1 August 1991 (1991-08-01), pages 427-429, XP000233400,**
- **RIZZARDINI M ET AL: "Sex differences in the metabolism of hexachlorobenzene by rats and the development of porphyria in females", BIOCHEMICAL PHARMACOLOGY, ELSEVIER, US, vol. 31, no. 22, 15 November 1982 (1982-11-15), pages 3543-3548, XP023847998, ISSN: 0006-2952, DOI: 10.1016/0006-2952(82)90573-1 [retrieved on 1982-11-15]**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

Description**Field of the Invention**

5 [0001] This invention relates to the field of waste recycling, and in particular to a method of devulcanizing a cross-linked elastomer material, such as scrap from molding operations.

Background of the Invention

10 [0002] Devulcanization is a method of recycling waste thermoset elastomeric material to produce a material that can be revulcanized into useful products. A thermoset elastomer results from a polymer that is irreversibly cured. Prior art processes for devulcanization use chemical, ultrasonic, biological with microorganisms, mechanical, microwave or steam techniques.

15 [0003] One such mechanical process known as high shear mixing (HSM) provides extremely high levels of shear and extensional stress, thereby inducing chemical reactions in the material being processed. US patent no. 7,461,970, assigned to the applicant, describes such a process. It uses a mixing apparatus having two opposing mixing members rotatable relative to one another about an axis and that have facing surfaces which extend away from the axis to define a mixing chamber. An array of mixing formations on at least one of the surfaces acts to mix material and propel the material within the chamber toward the axis. This mechanical process has demonstrated the ability to un-crosslink thermoset elastomers using shear energy such that approximately 60% of the original physical properties of the materials are recovered.

20 [0004] Other mechanical processes include the step of adding chemicals to the material in the mixing chamber. However, these chemicals are extremely toxic and cause toxic gases to be emitted during the process. Today these processes are only used in countries where there are no controls on toxic emissions or enforceable regulations to protect the environment from such contamination.

25 [0005] WO 03/014206A1, assigned to the applicant describes a process for treatment of cross-linked elastomers such that a predetermined portion of the untreated material remains as vulcanized granules to thereby produce a flowable material comprising vulcanised elastomer dispersed in a matrix of devulcanized elastomer. CN1385461 and Mouri M "De-vulcanisation conditions and mechanical properties of re-vulcanised rubber for EPDM" (part II) (01.01.2000) describe regeneration of rubber.

Summary of the Invention

35 [0006] The inventors have found that the addition of a suitable catalyst with a thiol terminus to the mechanical process of high shear mixing has been shown to significantly improve the properties of materials recovered and approximately halve the processing time.

40 [0007] According to one aspect of the present invention there is provided a method of devulcanizing a thermoset sulphur cross-linked elastomer material, comprising subjecting a batch of the material to a mechanical mixing process in a high shear mixer at a temperature of less than 80°C in the presence of an amount of 0.5 to 2% by wt. of a non-toxic biological catalyst having a thiol terminus to restore the material to a pre-vulcanized state suitable for revulcanization into useful products.

45 [0008] According to another aspect of the present invention there is provided a method of devulcanizing a thermoset sulphur cross-linked elastomer material, comprising subjecting a batch of the material to a mechanical mixing process in a high shear mixer at a temperature of less than 80°C in the presence of an amount of 0.5 to 2% by wt. of cystine to restore the material to a pre-vulcanized state suitable for revulcanization into useful products.

[0009] By biological catalyst is meant a catalyst obtained from a biological source, such as hair. Amino acids with thiol groups represent a suitable biological source. A preferred catalyst is L-cysteine. The addition of such a catalyst can improve the properties by as much as 12.5% and reduce the processing time by 50%.

50 [0010] The amount of 0.5 to 2 % by weight was selected as a range because this is the typical dosage of sulphur in a rubber compound, and the amount of biological catalyst was selected to match this dosage.

[0011] Biological catalysts are non-toxic, readily available and cost effective at the percentage and do not cause re-cure of the rubber without planned addition of rubber accelerators. They are effective at modest temperatures, < 80°C, and preferably in the range 25 - 40°C. If the temperature of the devulcanization process exceeds about 80°C, the material may revulcanize, thus defeating the object of the devulcanization process.

Detailed Description of Embodiments of the Invention

[0012] Figure 1 shows a high shear mixer (HSM) 100, of the type described in US patent no. 7,461,970. This device

was used to demonstrate the invention.

[0013] A first process was conducted using a control compound, 65A Natural Rubber, and using an accepted HSM protocol and then post processed sufficiently to produce a compoundable masterbatch.

[0014] Sulphur and rubber accelerator were added to achieve a curable control compound. The physical and rheological properties of the control compound were then assessed using a moving die rheometer.

[0015] A second process was conducted using the same control compound under the identical HSM and compounding protocol as used in the said first process. However, 1% by weight of L-Cysteine material was pre-dispersed in the said control compound during the HSM process immediately before the final plasticization step. The process was controlled within the temperature range of 25°C-80°C, the preferred temperature being 60°C.

[0016] A curable compoundable masterbatch was produced as a result. The same physical and rheological properties of said novel compoundable masterbatch were assessed to determine the effect of the addition of the catalyst - L-Cysteine.

[0017] The comparative results are shown below.

Cure Characteristics - MDR 6 mins @ 170°C		
Parameter	Control compound 65A natural rubber	Control compound plus 1% L-cysteine
ML	15.67	14.73
MH	27.88	27.37
TS2	0.56	0.46
TC50	1.1	0.58
TC90	1.34	1.21
Physical Properties - 20 min @ 150°C		
Parameter	Control compound 65A natural rubber	Control compound plus 1% L-cysteine
Tensile psi	2328	2620

2328 psi corresponds to 16.05 MPa and 2620psi corresponds to 18.06 MPa

Elongation %	231	246
Durometer A	66	67

[0018] The identified parameters have the following meanings:

MDR - moving die rheometer]

ML - minimum torque

MH - maximum torque

TS2 - scorch time (time to 2 point rise in torque on rheometer curve)

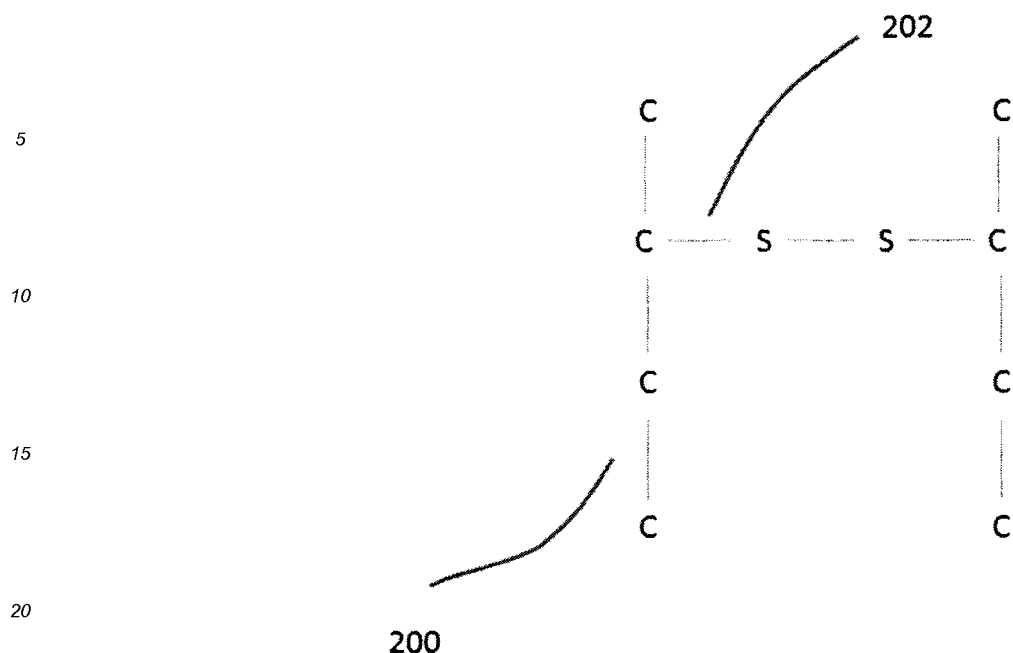
T50 - time to 50% of maximum cure MH

T90 - time to 90% of maximum cure.

[0019] Overall, a 12.5% improvement in physical properties and a reduced process time of about 50% was achieved. The first process took about ten minutes to process a batch size of 1.5Kg and the said second process took about five minutes to process the same batch size.

[0020] L-Cysteine is a naturally occurring amino acid and nutritional supplement. It is also used as an expectorant in medicine to liquefy mucous by breaking disulphide bonds in proteins. Since L-Cysteine is ingested by humans for medical purposes it is clearly non-toxic. Consequently, the use of L-Cysteine in an industrial process like devulcanization does not cause toxic emissions to be created by its use. Other generic homologues of cysteine may also be used as the catalyst in the process, including cystine, which is the product derived from the combination of two cysteine molecules to give an S-S bond.

[0021] The cross-linked chemical structure of a typical thermoset elastomer is as follows:



[0022] Chains, 200, of carbon atoms C are cross-linked to each other by chemical bonds, or crosslinks 202, with sulphur elements S.

[0023] By adding between 0.5% to 2%, the preferred embodiment being 1%, by weight of L-Cysteine to a natural rubber compound in the novel process the chemical bonds or cross links between the sulphur elements are targeted and weakened by the L-Cysteine. This causes more of these cross links to be selectively delinked, while the chemical bonds, or links, between the carbon elements are not weakened and remain strong. For this reason, the applicants believe that similar organic compounds with a thiol terminus will give the same or similar effects.

[0024] The mechanically applied shear energy severs more of the sulphur links 202 than carbon links thereby preserving more of the carbon chains 200. This in turn preserves more of the material's original properties and also allows the process to be completed in less time.

[0025] Also other biologically sourced organic chemicals that have thiol terminus-S-H can also be used as the catalyst in the process because they interact in a similar manner as L-cysteine through the thiol terminus and are inherently non-toxic.

[0026] The process is useful for devulcanizing cross-linked thermoset elastomer material, such as scrap rubber from molding operations. This rubber has a high value. The devulcanizing process restores the rubber to a pre-vulcanized state, wherein it may be revulcanized into useful products. Scrap rubber wastage from molding operations can be re-used. The invention is also applicable to scrap rubber from tires, although this is subject to a number of other treatments and is generally not as suitable for full recycling.

Claims

1. A method of devulcanizing a thermoset sulphur cross-linked elastomer material, **characterised by** subjecting a batch of the material to a mechanical high shear mixing process in a high shear mixer at a temperature of less than 80°C in the presence of an amount of 0.5 to 2% by wt. of a non-toxic biological catalyst having a thiol terminus to restore the material to a pre-vulcanized state suitable for revulcanization into useful products.
2. A method as claimed in claim 1, wherein the biological catalyst is an amino acid.
3. A method as claimed in claim 1, wherein the catalyst is cysteine.
4. A method as claimed in claim 2, wherein the catalyst is L-cysteine.
5. A method as claimed in claim 4, comprising about 1% by wt. L-cysteine.
6. A method as claimed in any one of claims 1 to 5, wherein the mixing process is carried out at temperature of about

60°C.

7. A method of devulcanizing a thermoset sulphur cross-linked elastomer material, **characterised by** subjecting a batch of the material to a mechanical high shear mixing process in a high shear mixer at a temperature of less than 80°C in the presence of an amount of 0.5 to 2% by wt. of cystine to restore the material to a pre-vulcanized state suitable for revulcanization into useful products.

8. A method as claimed in any one of claims 1 to 7, wherein the cross-linked elastomer material is scrap rubber.

Patentansprüche

1. Verfahren zur Entvulkanisierung eines duroplastischen schwefelvernetzten Elastomermaterials, **gekennzeichnet durch** Unterwerfen einer Charge des Materials einem mechanischen Hochschergeschwindigkeitsmischverfahren in einer Hochgeschwindigkeitsschermischvorrichtung bei einer Temperatur von weniger als 80 °C in Gegenwart einer Menge von 0,5 bis 2 Gewichtsprozent eines nichttoxischen biologischen Katalysators, der einen Thiolterminus aufweist, zum Zurückversetzen des Materials in einen vorvulkanisierten Zustand, der zum Wiedervulkanisieren in nützliche Produkte geeignet ist.

2. Verfahren nach Anspruch 1, wobei der biologische Katalysator eine Aminosäure ist.

3. Verfahren nach Anspruch 1, wobei der Katalysator Cystein ist.

4. Verfahren nach Anspruch 2, wobei der Katalysator L-Cystein ist.

5. Verfahren nach Anspruch 4, umfassend etwa 1 Gew.-% L-Cystein.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei der Mischvorgang bei einer Temperatur von etwa 60 °C durchgeführt wird.

7. Verfahren zum Entvulkanisieren eines duroplastischen schwefelvernetzten Elastomermaterials, **gekennzeichnet durch** Unterwerfen einer Charge des Materials einem mechanischen Hochschergeschwindigkeitsmischverfahren in einer Hochgeschwindigkeitsschermischvorrichtung bei einer Temperatur von weniger als 80 °C in Gegenwart einer Menge von 0,5 bis 2 Gew.-% Cystein, zum Zurückversetzen des Materials in einen vorvulkanisierten Zustand, der zum Wiedervulkanisieren in nützliche Produkte geeignet ist.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei das vernetzte Elastomermaterial Altgummi ist.

Revendications

1. Procédé de dévulcanisation d'un matériau élastomère réticulé thermodurci à base de soufre, **caractérisé par** la soumission d'un lot du matériau à un procédé de mélange mécanique à cisaillement élevé dans un mélangeur à cisaillement élevé à une température inférieure à 80°C en présence d'une quantité de 0,5 à 2 % en pds d'un catalyseur biologique non toxique ayant une terminaison thiol pour restaurer le matériau au niveau d'un état pré-vulcanisé convenant à la revulcanisation en produits utiles.

2. Procédé tel que revendiqué selon la revendication 1, où le catalyseur biologique est un acide aminé.

3. Procédé tel que revendiqué selon la revendication 1, où le catalyseur est la cystéine.

4. Procédé tel que revendiqué selon la revendication 2, où le catalyseur est la L-cystéine.

5. Procédé tel que revendiqué selon la revendication 4, comprenant environ 1 % en pds de L-cystéine.

6. Procédé tel que revendiqué selon l'une quelconque des revendications 1 à 5, où le procédé de mélange est conduit à une température d'environ 60°C.

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7. Procédé de dévulcanisation d'un matériau élastomère réticulé thermodurci à base de soufre, **caractérisé par** la soumission d'un lot du matériau à un procédé de mélange mécanique à cisaillement élevé dans un mélangeur à cisaillement élevé à une température inférieure à 80°C en la présence d'une quantité de 0,5 à 2 % en pds de cystine pour restaurer le matériau jusqu'à un état pré-vulcanisé convenant à la revulcanisation en produits utiles.

8. Procédé tel que revendiqué selon l'une quelconque des revendications 1 à 7, où le matériau élastomère réticulé est un caoutchouc de rebut.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 7461970 B [0003] [0012]
- WO 03014206 A1 [0005]
- CN 1385461 [0005]



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Szahsdalmi igénypontok

1. Eljárás hőre keményedő kén-térhálósított elastomer anyag devulkanizálására, amelyre jellemző, hogy az anyag adagját kitesztük mechanikus nagy nyírású keverő eljárásnak nagy nyírású keverőben kisebb, mint 80°C hőmérsékleten 0,5-2 tömeg% mennyiségű nem toxikus biológiai katalizátor jelenlétében, amelynek től vége van, hogy helyreállítsa az anyagot elővulkanizált állapotba, amely alkalmas újravulkanizálásra hasznos termékeké.
2. Az 1. igénypont szerinti eljárás, ahol biológiai katalizátor aminosav.
3. Az 1. igénypont szerinti eljárás, ahol katalizátor cisztein.
4. A 2. igénypont szerinti eljárás, ahol a katalizátor L-cisztein.
5. A 4. igénypont szerinti eljárás, amely körülbelül 1 tömeg% L-ciszteint tartalmaz.
6. Az 1-5. igénypontok bármelyike szerinti eljárás, ahol a keverési eljárás körülbelül 60°C hőmérsékleten van megvalósítva.
7. Eljárás hőre keményedő kén-térhálósított elastomer anyag devulkanizálására, amelyre jellemző, hogy az anyag adagját kitesztük mechanikus nagy nyírású keverő eljárásnak nagy nyírású keverőben kisebb, mint 80°C hőmérsékleten 0,5-2 tömeg% mennyiségű cisztin jelenlétében, hogy helyreállítsa az anyagot elővulkanizált állapotba, amely alkalmas újravulkanizálásra hasznos termékeké.
8. Az 1-7. igénypontok bármelyike szerinti eljárás, ahol térhálósított elastomer anyag használt gumi.