



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2856319 C 2015/06/02

(11)(21) **2 856 319**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

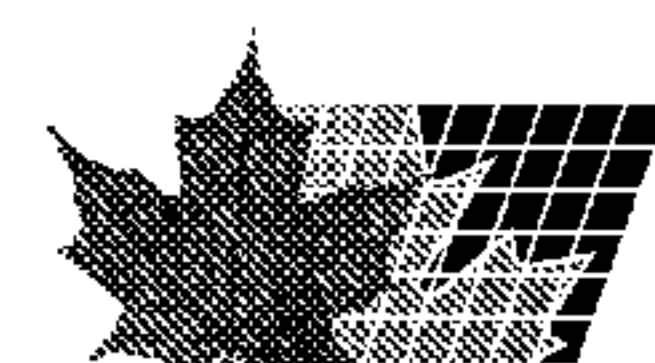
(86) **Date de dépôt PCT/PCT Filing Date:** 2012/11/19
(87) **Date publication PCT/PCT Publication Date:** 2013/05/30
(45) **Date de délivrance/Issue Date:** 2015/06/02
(85) **Entrée phase nationale/National Entry:** 2014/05/20
(86) **N° demande PCT/PCT Application No.:** CA 2012/001063
(87) **N° publication PCT/PCT Publication No.:** 2013/075216
(30) **Priorité/Priority:** 2011/11/25 (US13/304,509)

(51) **Cl.Int./Int.Cl. C08J 11/18** (2006.01),
C08C 19/08 (2006.01)
(72) **Inventeur/Inventor:**
FISHER, JAMES F., CA
(73) **Propriétaire/Owner:**
NEW RUBBER TECHNOLOGIES HOLDINGS, INC., US
(74) **Agent:** MARKS & CLERK

(54) **Titre : PROCEDE DE DEVULCANISATION D'UN MATERIAU ELASTOMERE RETICULE**
(54) **Title: METHOD OF DEVULCANIZING A CROSS-LINKED ELASTOMERIC MATERIAL**

(57) **Abrégé/Abstract:**

A thermoset cross-linked elastomer material, such as scrap tire rubber, is devulcanized by subjecting the material to a mechanical mixing process in the presence of 0.5 to 2% by wt. of an organic catalyst having a thiol terminus.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
30 May 2013 (30.05.2013)

(10) International Publication Number
WO 2013/075216 A1

- (51) International Patent Classification:
C08J 11/18 (2006.01) C08C 19/08 (2006.01)
- (21) International Application Number:
PCT/CA2012/001063
- (22) International Filing Date:
19 November 2012 (19.11.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
13/304,509 25 November 2011 (25.11.2011) US
- (71) Applicant: WATSON BROWN HSM LTD. [CA/CA];
6074 Shawson Drive, Mississauga, Ontario L5T 1E6 (CA).
- (72) Inventor: FISHER, James F.; 2953 Concession 11 South,
Singhampton, Ontario N0C 1M0 (CA).
- (74) Agents: MITCHELL, Richard et al.; c/o Marks & Clerk
Canada, PO Box 957, Station B, Ottawa, Ontario K1P 5S7
(CA).
- (81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,

- AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,
NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU,
RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ,
TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA,
ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).
- Published:
— with international search report (Art. 21(3))

WO 2013/075216 A1

- (54) Title: METHOD OF DEVULCANIZING A CROSS-LINKED ELASTOMERIC MATERIAL
- (57) Abstract: A thermoset cross-linked elastomer material, such as scrap tire rubber, is devulcanized by subjecting the material to a mechanical mixing process in the presence of 0.5 to 2% by wt. of an organic catalyst having a thiol terminus.

Method of Devulcanizing a Cross-linked Elastomeric Material

Field of the Invention

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

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.

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.

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.

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.

Summary of the Invention

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.

According to the present invention there is provided a method of devulcanizing a thermoset cross-linked elastomer material, comprising subjecting the material to a mechanical mixing process at a temperature of less than 80°C in the presence of an amount of 0.5 to 2% by wt. of a biological catalyst having a thiol terminus.

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%.

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.

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, $< 80^{\circ}\text{C}$, and preferably in the range 25 - 40°C . If the temperature of the devulcanization process exceeds about 80°C , the material may re-vulcanize, thus defeating the object of the devulcanization process.

In one aspect, there is provided a method of devulcanizing a thermoset cross-linked elastomer material, comprising 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 biological catalyst having a thiol terminus to restore the material to a pre-vulcanized state suitable for revulcanization into useful products.

In another aspect, there is provided a method of devulcanizing a thermoset cross-linked elastomer material, comprising 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 L-cysteine to restore the material to a pre-vulcanized state suitable for revulcanization into useful products.

In another aspect, there is provided a method of devulcanizing a thermoset cross-linked elastomer material, comprising 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.

Brief Description of the Drawings

The invention will now be described in more detail, by way of example only, with reference to the accompanying drawings, in which:

FIG. 1 is a schematic view of a high shear mixer,

FIG. 2 is a chart comparing physical and rheological properties of compounds; and

FIG. 3 is a schematic chemical structure of a cross-linked thermoset elastomer.

Detailed Description of Embodiments of the Invention

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.

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.

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.

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.

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.

Figure 2 shows the comparative results.

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.

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.

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.

The cross-linked chemical structure of a typical thermoset elastomer is seen in Figure 3.

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

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.

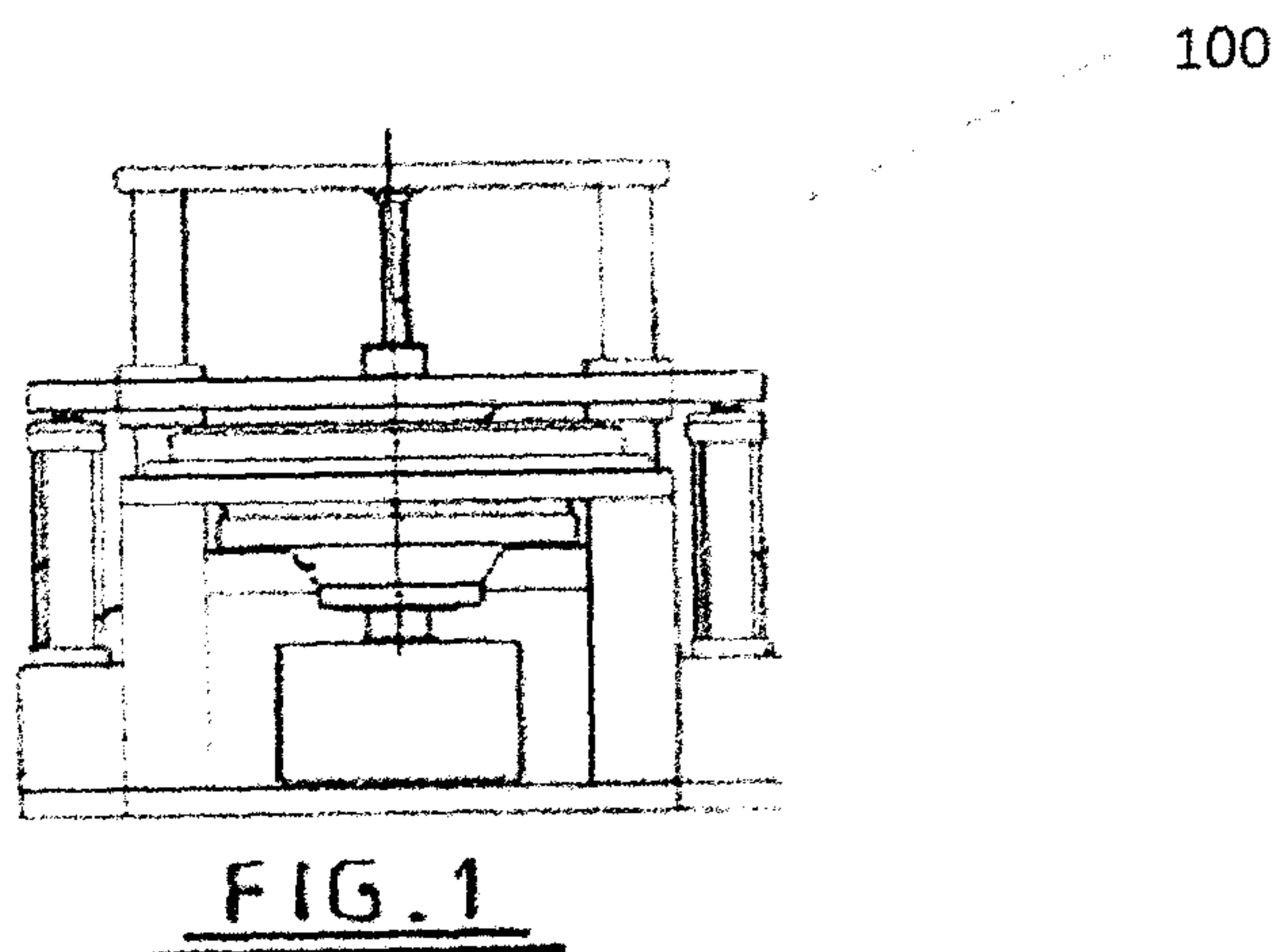
The mechanically applied shear energy severs more of the sulphur links 202 than carbon links thereby preserving more of the carbon chains 200. This in turn preserves more of the material's original properties and also allows the process to be completed in less time.

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.

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.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of devulcanizing a thermoset cross-linked elastomer material, comprising 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 biological catalyst having a thiol terminus to restore the material to a pre-vulcanized state suitable for revulcanization into useful products.
2. The method as claimed in claim 1, wherein the biological catalyst is an amino acid.
3. The method as claimed in claim 1, wherein the catalyst is cysteine.
4. The method as claimed in claim 3, comprising about 1% by wt. L-cysteine.
5. A method of devulcanizing a thermoset cross-linked elastomer material, comprising 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 L-cysteine to restore the material to a pre-vulcanized state suitable for revulcanization into useful products.
6. The method as claimed in claim 5, wherein the mixing process is carried out at temperature of about 60° C.
7. A method of devulcanizing a thermoset cross-linked elastomer material, comprising 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. The method as claimed in any one of claims 1 to 7, wherein the cross-linked elastomer material is scrap rubber.



Cure Characteristics - MDR 6 min @ 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
Elongation %	231	246
Durometer A	66	67

Figure 2

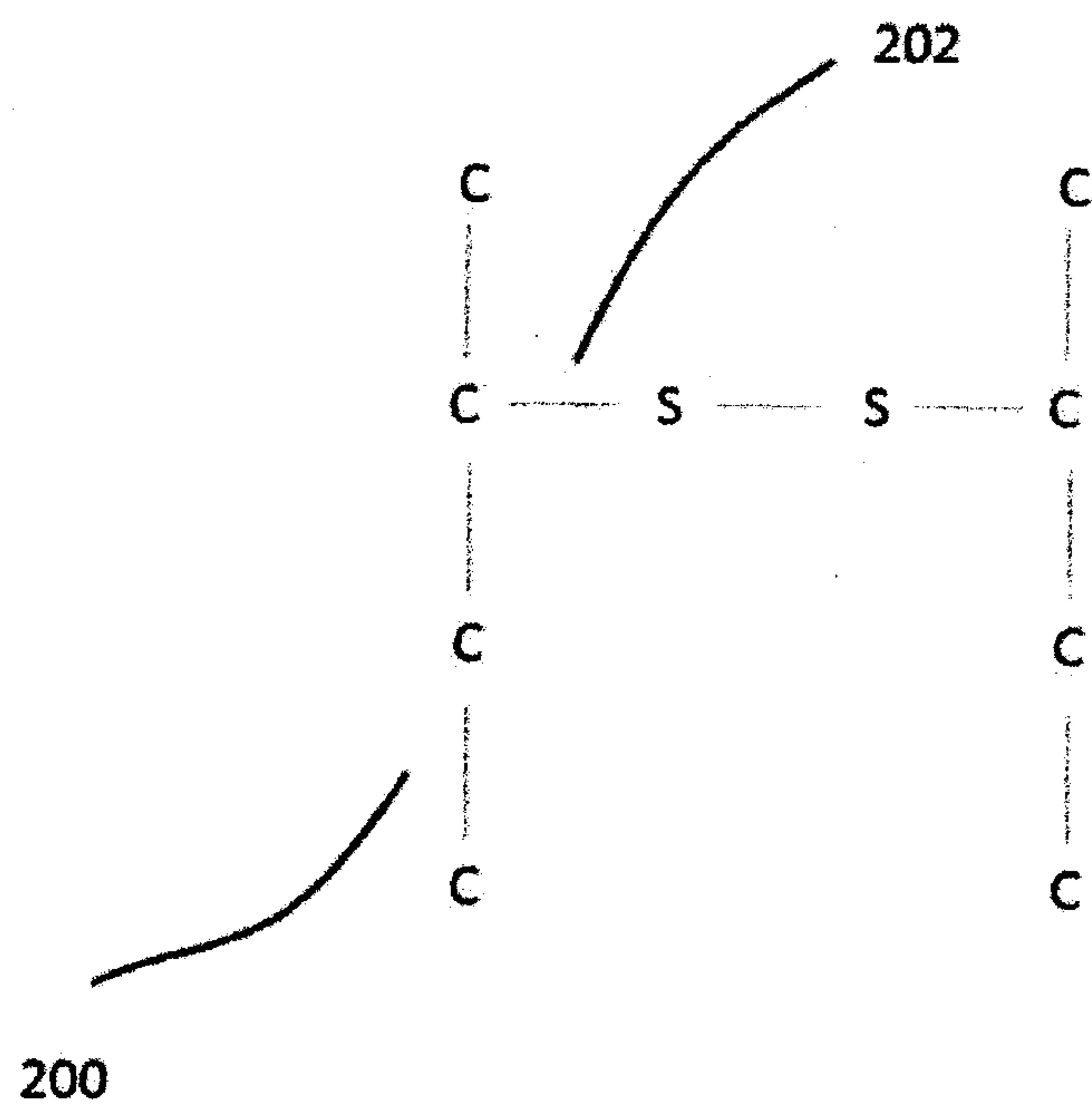


Figure 3