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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 February 2003 (20.02.2003)

PCT

(10) International Publication Number
WO 03/014206 A1

(51) International Patent Classification[7]: C08J 11/10, B29B 17/00

(21) International Application Number: PCT/GB02/03477

(22) International Filing Date: 29 July 2002 (29.07.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0119102.2 3 August 2001 (03.08.2001) GB

(71) Applicant *(for all designated States except US)*: **WATSON BROWN HSM LTD.** [GB/GB]; First Floor 59-61, High Street West, Glossop, Derbyshire SK13 8AZ (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BROWN, Christopher** [GB/GB]; Watson Brown HSM Ltd., First Floor 59-61, High Street West, Glossop, Derbyshire SK13 8AZ (GB). **BROWN, David** [GB/GB]; Watson Brown HSM Ltd., First Floor 59-61, High Street West, Glossop, Derbyshire SK13 8AZ (GB). **HODGKINSON, Nigel** [GB/GB]; Watson Brown HSM Ltd., First Floor 59-61, High Street West, Glossop, Derbyshire SK13 8AZ (GB). **WATSON, William, Ferguson** [GB/GB]; Watson Brown HSM Ltd., First Floor 59-61, High Street West, Glossop, Derbyshire SK13 8AZ (GB).

(74) Agent: **HOLMES, Mattew, Peter**; Marks & Clerk, Sussex House, 83-85 Mosley Street, Manchester M2 3LG (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/014206 A1

(54) **Title:** TREATMENT OF CROSS-LINKED ELASTOMERS

(57) **Abstract:** A method of treating (recycling) cross-linked elastomeric material comprises, subjecting the material to mechanical stresses in a processing apparatus to mechanochemically de-vulcanise a portion of the material. The processing operation is controlled such that a predetermined portion of the untreated material remains vulcanised as granules, to thereby produce a flowable material comprising granules of vulcanised elastomer disperses in a matrix of de-vulcanised elastomer.

TREATMENT OF CROSS-LINKED ELASTOMERS

The present invention relates to the treatment of cross-linked elastomers, and in particular vulcanised rubber (both natural and synthetic, and not limited to vulcanisation with sulphur), and to products produced from such treated materials. In particular, the invention relates to the re-cycling of rubber products, such as for instance vehicle tyres.

The need for effective re-cycling of rubber products is a recognised global problem. However, because of difficulties associated with de-vulcanising rubber (i.e. breaking the cross-links which join the polymer chains) scrapped rubber, and in particular scrapped tyres, has traditionally been landfilled or stock piled. This raises significant environmental concerns and thus there is an increasing demand to find new and improved ways of disposing of scrapped rubber, in some instances required by government legislation.

There are known methods of recycling scrap rubber which combine chemical and mechanical treatments to attempt to reverse the vulcanisation process and provide a soluble flowable material which can be re-cured and reused. However, such processes are relatively expensive and the materials they produce generally have significantly diminished physical and mechanical properties compared to the original product. In addition the chemicals used must be appropriate to the cross-linking mechanism of the material which therefore needs to be identified.

Accordingly, one of the most widely used methods to generate usable material from scrap rubber (such as scrap vehicle tyres) is to chop and grind the rubber into small granules or fine powders. Fine powders may be incorporated at relatively low levels into new rubber products (sometimes after additional chemical treatment to improve the material properties). A major area of application for granulated material derived from such scrap rubber is in the production of articles such as tiles, mats or other ground surfaces (often used in school playgrounds and athletic tracks) in which the granulated rubber crumb is combined with, and encapsulated by, a binder matrix (such as urethane) which is cured to bind the granules together in a suitable moulded or otherwise formed product. However, a significant disadvantage of this approach is the cost of the binder material which, given the very low cost of scrap rubber, can constitute the majority of the product cost.

It is an object of the present invention to obviate or mitigate the above disadvantages.

According to a first aspect of the present invention there is provided a method of treating cross-linked elastomeric material, the method comprising:

subjecting the material to mechanical stresses in a processing apparatus to mechanochemically de-vulcanise a portion of the material; and

controlling the processing operation such that a predetermined portion of the untreated material remains vulcanised as granules, to thereby produce a flowable material comprising granules of vulcanised elastomer dispersed in a matrix of de-vulcanised elastomer.

The mechanical stresses will generally be shear and/or extensional stresses.

According to a second aspect of the present invention there is provided a product formed from a treated material obtained, or obtainable from, the method according to the first aspect of the invention.

The predetermined portion of untreated material remaining vulcanised in the treated material need not be predetermined precisely. For instance the predetermination may be to specify an approximate amount, a maximum amount and/or a minimum amount of material to be de-vulcanised.

A major application of the present invention is in the re-cycling of re-claimed rubber but the invention may be applied to the treatment of any elastomeric material which responds to mechanochemical processing.

The treated material can be readily re-constituted by a simple curing process to re-cure the de-vulcanised material and the resultant products may be completely homogeneous. The treated material may be mixed with additional material prior to curing. Such additional material may include cured elastomers or elastomer that has not previously been vulcanised and which may be cured together with the treated elastomer in a single stage.

Mechanochemistry is essentially a process of inducing chemical reactions in a material solely by the application of mechanical stresses. One significant advantage of mechanochemistry is that there is no need to identify the nature of the cross-links as would be required for chemical de-vulcanisation. Mechanochemistry has for many years been applied to non-vulcanised rubber stock as a means for modifying (usually reducing) the molecular weight of the polymer to facilitate easy processing. Typically, the required stresses are imparted to the material in a machine such as a two-roll mill.

Mechanochemistry has also been proposed as a method of solubalising re-claimed rubber. Such a process is disclosed in UK patent number 2,300,129 by William Watson. In his patent, William Watson discloses a method of re-claiming rubber by mechanically mixing the re-claimed material with a minor amount of raw rubber which provides a matrix into which rubber de-vulcanised by the mixing stresses dissolves. The result is a flowable material with properties very close to those of raw rubber which can then be re-cured, and otherwise treated, in conventional ways to produce products having substantially the same properties as the original product.

The present invention takes advantage of the possibilities offered by mechanochemistry in producing predictable changes to the chemical nature of a cross-linked elastomer by appropriate control of the processing conditions. In particular, the invention recognises that rather than applying mechanochemistry to produce fully de-vulcanised product, the conditions can be controlled to produce a material comprising partly de-vulcanised rubber and partly granules or particles of the original re-claimed rubber.

In particular, by operating the process at temperatures below the curing temperature of the materials (the preferred temperatures for operation of the present invention are between 30 and 90°C), it can be ensured that any de-vulcanisation is due only to the mechanochemical process and not as a direct result of a temperature increase in the material. This ensures that those granules or particles of the original material which remain vulcanised are largely unaffected by the process and thus retain their original properties. However, surface regions of the vulcanised granules/particles generally will become tacky through at least partial de-vulcanisation by the mechanochemcial process. This is an additional advantage in that it improves the binding of the remaining vulcanised particles/granules.

For instance products produced from a re-cycled material obtained in accordance with the present invention may replace the urethane bound rubber granule products mentioned above. With the present invention, the proportion of de-vulcanised material acts to allow the material to flow (so that it may be processed in conventional rubber processing equipment) and also as a matrix which can be re-cured to bind the granules of rubber together thereby obviating the need to provide a separate binder such as the urethane binder mentioned above. Products according to the present invention are therefore cheaper to produce and posses better physical properties than the prior art products mentioned above.

The invention modifies the known mechanochemical process to reach a practical compromise between the required time and energy input in treating the re-claimed material and the usefulness of the final product. The products of the present invention also tend to be stronger and more robust than the prior art materials formed using a urethane binder material.

The method in accordance with the present invention may be controlled to vary the amount of the original material which is de-vulcanised and the amount which remains as vulcanised granules. Products of quite different physical characteristics can thereby be produced from treated material in accordance with the present invention.

The portion of the original material which is de-vulcanised should preferably be sufficient to ensure that the treated material is sufficiently flowable to allow subsequent processing using conventional rubber processing equipment. The de-vulcanised portion of the material is therefore preferably at least 10% of the material (by weight) although it may well be more than 90%.

The proportion of de-vulcanised material to vulcanised granules has an effect on the density of products made from the treated material. Thus, for applications such as impact absorbing tiles or the like the portion of de-vulcanised material should preferably be between 10% and 75% of the material (by weight).

The size of the granules in the un-vulcanised portion of the material also has an effect on the characteristics of the treated material, and thus products made from that material. This can also be varied by appropriate control of the mixing process. It is envisaged that for most commercial applications of the treated material (for instance for the production of impact absorbing tiles) the granule size should be less than about 15mm and preferably less than 10mm (e.g. of the order of 0.8 to 7mm).

The treated material according to the present invention may be formed (e.g. moulded or extruded) and cured in accordance with entirely conventional methods. For instance, the material could be cured and moulded in a single process, in a press for example. Moreover, the bulk density of the final product can further be varied by controlling the fill-in factor of the mould and the forming process. The material can, for instance, be compressed to reduce the number or size of voids (i.e. air spaces formed at the granule sites) to increase density.

Depending on the type of mixer used to apply the required stresses to the original vulcanised material (e.g. re-claimed rubber etc), in untreated form the material may be in sheets, slabs, granules, irregular sized and shaped fragments etc. No particular pre-processing is required The material should, however, be as free from unwanted contaminants as possible. For instance, if the untreated material is re-claimed rubber from scrap tyres, all metal should preferably be removed from the material. However, this is not essential as the de-vulcanised material can serve to bind such contaminants into the final product.

A further important advantage of the present invention is that there is no requirement to mix the original vulcanised material with an amount of raw rubber or similar elastomer. Thus, the treated material of the present invention may be derived entirely from re-claimed material. Accordingly, products according to the present invention preferably comprise entirely re-cycled elastomer. Moreover, products of the present invention are themselves 100% re-cyclable by the method according to the present invention.

Although no chemicals are required for the de-vulcanising process (which is entirely mechanochemical), additives common to conventional rubber formulation technology may be added to the material, for instance to suit requirements of subsequent re-curing of the de-vulcanised portion of the material (which may be based on any conventional curing system such as, but not limited to, one utilising sulphur as a vulcanising agent).

Various different forms of mixer could be used to impart the required stresses on the material in the mixing process of the present invention. For instance, the material could be cycled through a conventional two-roll mill. However, UK patent number 2,300,129 mentioned above discloses a form of mixer specifically designed for mechanochemistry. The mixer generally moves the material through a series of high stress and relaxation zones whilst an integrated cooling system maintains optimum mixing temperatures. The basic high shear mixer described in this patent has been further developed by Watson Brown HSM Limited which produces mixers suitable for operation of the present invention.

Essentially, the mixer comprises a first member that is mounted for movement relative to a second member and has a grooved surface that is opposed to, and separated by a gap from, a grooved surface of the second member. The arrangement is such that one or more grooves and lands of each grooved surface are traversed within the gap by one or more grooves and lands of the other surface during movement of the first member for shearing and splitting material entered into the gap. Each groove has walls that are inclined both to the respective grooved surface and outwardly from one another upwardly of the groove. The grooves are also configured to draw material entering the gap progressively further in to the gap forcing it along the grooves to well up for mixing distributively with material moving backwardly of the grooves in the gap.

Reference may be made to UK patent number 2,300,129 for further details of the basic configuration of the mixer.

A further advantage of the above form of mixer is that the temperature of the material being mixed can be readily controlled by way of an integral water cooling system. For instance, by maintaining temperatures below a curing temperature curatives can be introduced during the high stress mechanochemical process without any danger of the material actually curing within the mixer. This obviates the need to provide a separate mixing stage for addition of a curative (e.g. vulcanising agent such as sulphur) to the material after it has been subjected to the mechnochemical mixing process. This is in addition to the advantages of low temperature operation mentioned above.

The present invention will now be further exemplified by specific example.

Example

Granulated rubber re-claimed from scrap tyres was mixed in a Watson Brown HMS Limited high shear mixer. The untreated material supplied to the mixer comprised granules of between 3mm and 7mm diameter. The material in the mixer was maintained at a temperature below 80°C (and preferably below 60°C) by the re-circulating water cooling system.

The mixing was stopped before all of the material had been de-vulcanised, so that a portion of the original material remained as granules (of a size of approximately 7mm) dispersed within a matrix of well fluidised material.

The treated material was then transferred to a conventional two-roll mill where curatives were added (i.e. sulphur and associated accelerators). The material was then moulded by conventional means, using a heated press. In one specific example 0.5-2% sulphur was added to the treated material which was then cured at 150°C for 10 to 30 minutes.

A range of products were produced from the treated material having a density determined primarily by the fill factor of the mould, ranging from a relatively soft compressible material (which typical may be porous) to a substantially solid article.

The final product may be coloured on one or more of its surfaces by the use of a coloured material, which may be derived entirely from re-cycled rubber having been generated by the process according to the present invention. The covered layer may thus be co-moulded along with the bulk of the material. Alternatively, appropriate pigments could be added to the material before it is cured.

It will be appreciated that although the invention has been described above with particular with regard to re-cycling rubber products, such as scrap tyres, the invention can be applied to the treatment of any vulcanised elastomer which responds to mechanochemical stressing. The range of materials which could be treated in accordance with the present invention, and the products which could be made from material treated in accordance with the present invention, will be readily apparent to the appropriately skilled person.

CLAIMS

1. A method of treating cross-linked elastomeric material, the method comprising:

subjecting the material to mechanical stresses in a processing apparatus to mechanochemically de-vulcanise a portion of the material; and

controlling the processing operation such that a predetermined portion of the untreated material remains vulcanised as granules, to thereby produce a flowable material comprising granules of vulcanised elastomer dispersed in a matrix of de-vulcanised elastomer.

2. A method according to claim 1, wherein the portion of de-vulcanised material is at least 10% of the treated material.

3. A method according to claim 1 or claim 2, wherein the granules have a maximum diameter of about 15mm.

4. A method according to claim 1 or claim 2, wherein the granules have a maximum diameter of about 10mm.

5. A method according to claim 1 or claim 2, wherein the granules have a diameter in a range between about 0.8mm and 7mm.

6. A method according to any preceding claim, wherein the treated material is formed and cured to produce a product of a predetermined density.

7. A method according to claim 6, wherein the density is at least in part controlled by appropriate control of pressure applied to the material as it is formed.

8. A method according to claim 6 or claim 7, wherein the treated material is formed in a mould, and the density of the material is at least in part determined by controlling the fill-in factor of the mould.

9. A method according to any one of claims 6 to 8, wherein the product is an impact absorbing tile or mat or similar product suitable for use as a flooring material or as a covering material for a structure or as a shock absorbing component or structure.

10. A method according to any one of claims 6 to 9, wherein a curing agent is added to the material during the mechanochemical mixing process, and the material is cooled during said mixing to maintain it at a temperature below the curing temperature.

11. A method according to any preceding claim, wherein the untreated material is a re-claimed material.

12. A method according to claim 10, wherein the untreated material is re-claimed rubber.

13. A method according to claim 11, wherein at least a portion of the untreated material comprises rubber re-claimed from scrap vehicle tyres.

14. A method according to any preceding claim, wherein the untreated material comprises entirely of vulcanised elastomer.

15. A method according to claim 14, wherein the untreated material comprises entirely of re-claimed elastomer.

16. A product formed from material treated in accordance with any preceding claim.

17. A product formed from a material obtainable by a method according to any preceding claim.

18. A product comprising discrete granules of re-claimed elastomer dispersed in a matrix of said elastomer which has been de-vulcanised and re-cured.

19. A product according to claim 18, wherein all of the elastomeric material is re-claimed material.

20. A method of treating cross-linked elastomers, substantially as hereinbefore described.

21. A method of re-cycling elastomeric material, substantially as hereinbefore described.

22. A method of re-cycling rubber re-claimed from scrap vehicle tyres, substantially as hereinbefore described.

23. A product formed from re-claimed elastomeric material, substantially as hereinbefore described.

INTERNATIONAL SEARCH REPORT

PCT/GB 02/03477

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J11/10 B29B17/00

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 C08J B29B

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)

PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 01, 29 January 1999 (1999-01-29) & JP 10 287765 A (YAMABISHI IND CO LTD), 27 October 1998 (1998-10-27) abstract ---	1-23
X	RU 2 098 275 C (ARKHTEKHSTROM FA) 10 December 1997 (1997-12-10) abstract ---	1-23
X	RU 2 098 272 C (ARKHTEKHSTROM FA) 10 December 1997 (1997-12-10) abstract ---	1-23
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 October 2002	17/10/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Kofoed, J

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 1 201 390 A (TOYOTA MOTOR CO LTD ;TOYODA GOSEI KK (JP); TOYODA CHUO KENKYUSHO K) 2 May 2002 (2002-05-02) claim 1; figure 1; examples 1-4	1-23
X	WO 95 04640 A (MOVETECH INC) 16 February 1995 (1995-02-16) page 2, paragraph 3 page 9, paragraph 1	1-23
X	US 5 904 885 A (ARASTOOPOUR HAMID ET AL) 18 May 1999 (1999-05-18) column 1, line 13-16; example 1	1-23
X	WO 01 23464 A (NOORDERMEER JACOBUS WILHELMUS ;DOES LEEN V D (NL); DSM NV (NL); DU) 5 April 2001 (2001-04-05) page 2, line 14-18; claim 1	1-23
X	EP 0 997 252 A (BRIDGESTONE CORP) 3 May 2000 (2000-05-03) page 3, line 10-33	1-23
X	EP 0 887 372 A (TOYOTA MOTOR CO LTD ;TOYODA GOSEI KK (JP); TOYODA CHUO KENKYUSHO K) 30 December 1998 (1998-12-30) claim 3	1-23
A	DE 41 04 435 A (BAYER AG) 20 August 1992 (1992-08-20) claim 1	6-9

INTERNATIONAL SEARCH REPORT

PCT/GB 02/03477

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 10287765	A	27-10-1998	NONE		
RU 2098275	C	10-12-1997	RU 2098275	C1	10-12-1997
RU 2098272	C	10-12-1997	RU 2098272	C1	10-12-1997
EP 1201390	A	02-05-2002	EP 1201390	A1	02-05-2002
			WO 0074914	A1	14-12-2000
WO 9504640	A	16-02-1995	AU 7379394	A	28-02-1995
			WO 9504640	A1	16-02-1995
US 5904885	A	18-05-1999	AU 1622099	A	16-06-1999
			WO 9928105	A1	10-06-1999
WO 0123464	A	05-04-2001	NL 1013155	C2	29-03-2001
			AU 7458100	A	30-04-2001
			AU 7458300	A	30-04-2001
			EP 1226207	A1	31-07-2002
			WO 0123464	A1	05-04-2001
			WO 0123465	A1	05-04-2001
			NL 1015003	C2	29-03-2001
EP 0997252	A	03-05-2000	JP 2000127162	A	09-05-2000
			JP 2000128901	A	09-05-2000
			EP 0997252	A2	03-05-2000
			US 6335377	B1	01-01-2002
EP 0887372	A	30-12-1998	EP 0887372	A1	30-12-1998
			JP 3272623	B2	08-04-2002
			JP 9227724	A	02-09-1997
			US 6133413	A	17-10-2000
DE 4104435	A	20-08-1992	DE 4104435	A1	20-08-1992