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(71) **Applicant** *(for all designated States except US)*: **TYRE RECLAMATION SERVICES INTERNATIONAL LIMITED** [NZ/NZ]; 73a Webster Avenue, Mt Roskill, Auckland 1041 (NZ).

(72) **Inventor; and**
(75) **Inventor/Applicant** *(for US only)*: **WESTBROOK, Dennis Brian** [ZA/NZ]; Unit 1, 32 Eastern Beach Rd, Eastern Beach, Manukau 2012, Auckland (NZ).

(74) **Agent**: **SIMS, Antonia Luz Ines**; PO Box 15-520, 160 Killarney Road, Dinsdale 3243, Hamilton (CA).

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(54) **Title**: IMPROVEMENTS IN & RELATING TO TYRE RECYCLING

(57) **Abstract**: The present invention processes rubber products, such as from tyres, according to a process in which an extractant is introduced to the rubber material and subjected to a wet milling process to create a slurry-like material. Volatile distillate fractions are recovered from the slurry which may be used as a fuel. Further heating can produce substantially dry carbon rich product, which can be similar in character to pyrolytic carbon.

IMPROVEMENTS IN & RELATING TO TYRE RECYCLING

FIELD OF INVENTION

The present invention is directed to methods of recycling tyres comprising the extraction of organic hydrocarbons and volatiles, the process typically yielding a volatile product fraction and a carbon rich product.

BACKGROUND DESCRIPTION

A significant worldwide problem is that of rubber tyres from vehicles. They are difficult or expensive to recycle, and most are burnt (giving rise to pollution issues) or buried as landfill with a small portion converted into novel uses or subjected to expensive recovery methods.

Part of the problem is that most vehicle tyres are highly modified polymers and copolymers which have been optimised for vehicle use – notably toughness, longevity in use, traction, and resistance to chemicals. As a consequence used tyres are not easy to break down or convert into usable materials. The presence of steel belts in the majority of tyres also adds a further problem and limits available recycling options. The present invention seeks to consider both the rubber materials of items such as tyres, as well as tyres in which steel is present.

Many tyres are shredded, primarily to reduce the bulk of the original tyre for landfill applications, and to further facilitate any further mechanical processes involving the tyre. Typical shredded tyre pieces still have the steel from belts embedded in the rubber (which can limit use of the shredded material). The typical size of shredded tyres can vary, though are typically of an average particle size of 100mm or less and nominally around 50mm. The present invention considers the use of readily available shredded tyre material, and rubber crumb which is sometimes produced therefrom.

The problem which then remains is how to convert the rubber material into something useful. Tyres are carbon rich and often contain extractable organic fractions. As both are a commodity of value, there is some considerable benefit in the recovery of either or both. The recovery of saleable portions is also attractive as the alternative, disposal, usually represents a cost. Consequently some processes have been developed in the art to process tyres and comminuted material therefrom.

One method is pyrolysis in which rubber materials (and other materials including plastics, carbon rich waste, etc.) are pyrolised at high temperature in a chamber. Volatiles released during pyrolysis may be recovered. US Patent 5411714 by Wu is an example of such a process. The problem however is that pyrolysis is typically an energy expensive method, and can take a while to perform each batch. Given the current stockpile of tyres, and the rate this is growing, a faster and more energy process would represent a significant commercial advantage. Being able to isolate and recover usable volatile fractions (rather than burning these to create energy for a pyrolysis process, or scrubbing these off as waste products) yields a commercial valuable product and thus their efficient recovery as a commodity represents a further commercial advantage.

There is significant art on pyrolysis techniques (e.g. US 4389151, US 5085738, and US 4038100) though most look at improving the efficiency of the pyrolysis technique or apparatus associated therewith. They all represent energy-inefficient techniques.

Another group of methods practised in the art are catalytic hydrocracking processes (e.g. US4865625 and US4251500) though require a significant investment in plant and can again be expensive or uneconomic to operate.

As a departure, Dobozy in US Patent US6722593 and related patent US5316224 introduces a non-pyrolytic method. Here tyre pieces are pre-soaked for an extended period of time (e.g. 24 hours) to soften them. When suitably softened the pieces are milled into a smaller size, and then volatile fractions distilled using an industrial microwave for heating. This continues until a solid residue remains which is a usable carbon rich commodity.

Dobozy's work shows some promise as it can recover volatile fractions from the tyre, and which can be used as a saleable commodity. However there are a number of potential problems the current applicant considers limits it from being a viable commercial process. Firstly is the length of time required for pre-softening the rubber material. For an industrial scale process this would involve a huge number of large storage vats and large quantities of solvent (expense, and safety issues). Secondly, there is still essentially a large amount of energy consumed in the final heating stages. Finally, the process is not easily amenable to a continuous process, and would be rather slow as a batch process. If one considers the economics of throughput against capital expense of plant and materials, there are potential limitations associated with the method of Dobozy's patents.

Accordingly it would be commercially useful to devise a method for recovering useful or saleable commodities from waste rubber materials which possessed one or more of the following features: it did not rely solely on high energy use pyrolytic methods; it was relatively fast in its process time from raw material to product; and was amenable to a continuous process.

Therefore there is a need for an improved method of recycling and recovering useful commodities from rubber materials such as vehicle tyres.

It is an object of the present invention to consider and address one or more of the problems highlighted above..

It is also an object of the present invention to provide an improved process method for the recovery of useful commodities from rubber materials such as vehicle tyres.

At the very least it is an object of the present invention to provide the public with a useful alternative to the prior art.

Aspects of the present invention will be described by way of example only and with reference to the ensuing description.

GENERAL DESCRIPTION OF THE INVENTION

According to one aspect of the present invention there is provided a method for recycling rubber materials comprising steps of:

i) introducing rubber crumb into a shearing mill capable of a wet milling process;
ii) introducing at least one designated extractant to said rubber material so that milling occurs in the presence of said designated extractant;
iii) milling the rubber material to the size of reduced fines, as herein defined, to create a rubber slurry with said designated extractant;
iv) subjecting the rubber slurry to a heating stage to remove distillate fractions.

According to another aspect of the present invention there is provided a method for recycling rubber materials, substantially as described above, comprising the additional step of:

v) subjecting the residue fraction of step (iv) to a heating stage to create a substantially dry carbon rich product.

According to another aspect of the present invention there is provided a method, substantially as described above, which includes a preliminary step of producing rubber crumb from shredded rubber by a milling process which includes a non-shearing action.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the non-shearing milling process comprises a hammering or impacting action.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the non-shearing milling process comprises a hammer mill.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the non-shearing milling process is optimised to separate non-rubber materials embedded in, or attached to, the shredded rubber from the rubber materials therein.

According to another aspect of the present invention there is provided a method, substantially as described above, in which there is an additional step of separating non-rubber materials from the rubber crumb produced.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the separation process is a magnetic separation process.

According to another aspect of the present invention there is provided a method, substantially as described above, in which there is a drying step to remove water and moisture from the rubber crumb before it is subjected to a wet milling process.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the designated extractant is added to said rubber crumb once it is in the shearing mill.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the designated extractant is selected to act as a lubricant to rubber crumb being milled in the shearing mill.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the designated extractant comprises one or more members of any one or more subgroups in the group comprising: preferred hydrocarbon extracts, preferred organic extractants, and preferred plant based extractants.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the group of preferred hydrocarbon extractants comprises: halocarbons, halogenated hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons, substituted cyclic hydrocarbons, substituted aromatic hydrocarbons, cyclohexane, dichoromethane, trichloroethane, xylene, benzene, hexane, heptane, pentane, light naphthas and petroleum distillates, mineral turpentines, kerosenes; all having a boiling point of less than 190°C, and a melting point of less than 50°C at standard atmospheric pressure.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the group of preferred organic extractants comprises: ethers, ketones, aldehydes, diethyl ether, acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), butyraldehyde, aromatic and non-aromatic heterocylic compounds with rings comprising carbon and oxygen, dioxane, furan, tetrahydrofuran (THF), aromatic and non-aromatic heterocylic compounds with rings comprising carbon and nitrogen, pyridine, aromatic and non-aromatic heterocylic compounds with rings comprising carbon and sulfur, thiophene, alcohols, methanol; all having a boiling point of less than 250°C, and a melting point of less than 50°C at standard atmospheric pressure.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the group of preferred plant based extractants comprises: light vegetable oils, wood turpentines, wood alcohols, terpenes, pine oils, tall oils, oils extracted from wood, oils extracted from seeds, terpenoids, pinene, limonene, all having a boiling point of less than 250°C, and a melting point of less than 50°C at standard atmospheric pressure.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a temperature of 190°C or less

According to another aspect of the present invention there is provided a method, substantially as described above, in which prior to heating of the rubber slurry there is at least one mechanical separation step to separate liquid from solid components.

According to another aspect of the present invention there is provided a method, substantially as described above, in which a said mechanical separation step comprises one or more of: decanting, centrifuging, filtration, and fluid absorption into a medium from which it can be recovered.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the mechanical separation step comprises a pressurised filtration method.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a temperature of 140°C or less.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a temperature of 120°C or less.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a reduced pressure, which is less than atmospheric pressure.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a reduced pressure of 50 Torr or less.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a reduced pressure of 5 Torr or less.

According to another aspect of the present invention there is provided a method, substantially as described above, in which at least part of said distillate fractions are reintroduced as designated extractant into the shearing mill.

According to another aspect of the present invention there is provided a method, substantially as described above, in which said reintroduced distillate fractions comprise mainly recovered designated extractant from the rubber slurry.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the residue fraction occurs at a temperature exceeding 200°C.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the residue fraction occurs at a temperature exceeding 350°C.

According to another aspect of the present invention there is provided a method, substantially as described above, in which heating of the residue fraction occurs, for at least part of the time, at a reduced pressure.

According to another aspect of the present invention there is provided a method, substantially as described above, in which, when heating of the residue fraction occurs, distilled volatiles are collected.

According to another aspect of the present invention there is provided a method, substantially as described above, in which distilled volatiles are reintroduced to the rubber slurry and or distillate fractions occurring prior to the heating of the residue fraction.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the method is performed as a sequence of batch steps.

According to another aspect of the present invention there is provided a method, substantially as described above, in which the method is performed substantially as a continuous process.

Apparatus for performing the method substantially as described above, said apparatus comprising a shearing mill capable of wet processing, delivery means for rubber slurry produced by the shearing mill to a heating chamber, heating means for elevating the temperature of rubber slurry within the chamber, and distillation apparatus for recovering volatiles

According to another aspect of the present invention there is provided a method, substantially as described above, in which the same heating chamber is used for heating the slurry and residue fractions.

According to another aspect of the present invention there is provided a carbon rich solid product from the processing of rubber according to a method substantially as described above.

According to another aspect of the present invention there is provided a distilled product obtained from performing a method substantially as described above.

Definitions:

The term “rubber material” as used herein shall refer to (typically) elastomeric materials commonly referred to in the trade, or industry, as rubbers. It shall include materials derived from natural rubbers, modified natural rubbers, and synthetic rubbers. In particular it includes materials comprising, or at least partially derived from, monomers such as isoprene, chloroprene, butadiene, and isobutylene.

The term “rubber crumb” as used herein shall refer to rubber materials whose average particle size is 25mm or less or can pass through a 25mm mesh. More preferably, the average particle size is 10mm or less. The rubber crumb may, but not necessarily, be derived from tyres.

The term “shredded rubber” as used herein shall refer to rubber products and materials which have been comminuted to smaller than their original size, and/or screened to a threshold size. The threshold size is typically an average particle size of 200mm or less, or can pass through a 200mm mesh. The preferred size for the present invention is 75mm or less. The shredded rubber may include impurities of which the most typical is steel (steel belted tyres).

The term “reduced fines” as used herein shall refer to an average particle size of 100μm or less, more preferably 40μm or less, and even more preferably 20μm or less.

The term “rubber slurry” as used herein in shall refer to a composition containing liquid with solid particles substantially dispersed therein, and which may be gel-like (high viscosity) or fluid (lower viscosity) in nature.

The term “dry” as used herein shall mean substantially free of liquid, wherein liquid includes both aqueous and non-aqueous liquids.

The term “distillate fraction” as used herein shall mean a fraction recovered from a distillation process, or from a heated material.

The term “residue fraction” as used herein shall mean the fraction remaining after a distillate fraction has been removed.

A significant difference between the present invention and that of Dobozy is the elimination of pre-softening step prior to milling of the rubber material. In commercial terms this is significant as it potentially speeds the process considerably and eliminates the need for storing large quantities of raw material while it softens, as well as reducing the amount of fluid solvents used in the process. The present invention also avoids the hazards associated with storing large amounts of solvent and raw materials in holding vats.

Rather than pre-softening rubber material for a period of 4 hours or more (or requiring the introduction of heat to reduce this period), it has been found that an effective process can be performed by introducing a designated extractant at the time of milling by a shear mill.

While the designated extractant may be added immediately prior to introduction of the rubber material into the shearing mill, preferred embodiments introduce the rubber material to the designated extractant within the shearing mill itself. Preliminary experimentation provides the observation that the mechanical action of shearing the rubber material to a very fine size in the presence of a designated extractant appears to facilitate a more rapid action of the designated extractant on the rubber material, though the fine size of the resulting milled rubber material is possibly also partly responsible. While the exact mechanism is unknown, the surprising result is that a milling product (in the present case a slurry), from which volatiles can be readily extracted and a carbon rich product prepared, can be obtained in a time frame of tens of seconds to minutes, rather than the hours associated with the pre-soaking and shearing of Dobozy's raw material. This is a significant advance in terms of production processes.

In its simplest form, the invention comprises taking a rubber material (as herein defined) and shear milling it in the presence of a designated extractant as a wet milling process. The shear milling should reduce the rubber material particles to the size of reduced fines (as herein defined) and yield a slurry (also as herein defined). The viscosity of the slurry may be chosen to suit the design of the plant (apparatus) and pumping/conveying means. The slurry is then subjected to at least one heating step to remove volatiles as one or more distillate fractions. In preferred embodiments this heating step is characterised as being of relatively low temperature (particularly compared to pyrolysis methods) being typically of 190°C or less, more preferably 140°C or less and ideally 120°C or less, though this also depends on user choice regarding the nature of the distillate product, and partly also on the extractant used.

This distillation may occur under a reduced pressure. Subsequently the remaining residue fraction can be heated to a higher temperature to remove any final volatiles remaining (which one may not wish to include in the initial distillate fraction(s)) and to convert the residue essentially to a carbon rich product. This final stage is typically in excess of 200°C and typically around 350-400°C which is still low by pyrolysis standards. Prior to the final stage it appears that the combination of milling and chemical action of designated extractants has yielded a residue which is relatively easily converted to a carbon rich product (as opposed to the raw rubber material). The final stage may also be under a reduced pressure.

To give better context to the fuller invention, and by way of example only, we shall now describe a complete process embodiment which might start with whole tyres and other rubber waste, as well as some of the variations which might be implemented. This example includes steps which may not necessarily be included in some embodiments of the invention, but which are useful to include for the purpose of explanation.

The first step is the preparation of a suitable raw material. For large items such as tyres, initial comminution is typically performed. This may be by the common process of tyre shredding which produces shredded particles typically around 50-100mm average size. As the particles need to be made smaller to produce a rubber crumb (preferred raw material for shear milling) smaller sized shred particles are preferred. At this stage any steel belts are typically still embedded in the rubber, though some shredding machines do remove the steel reinforcing.

Next the shreds are introduced to impact milling apparatus (as opposed to shearing apparatus) to further reduce the particle sizes to that typical of rubber crumb. Typically a hammer mill will be used at this stage, though other mills can be considered. Ideally the hammering/impact of this stage helps separate the rubber (as a crumb) from any remaining steel (this also depends on whether the shredding process has already removed the steel). The resulting steel can be removed by a suitable method, such as magnetic separation. Steps to remove impurities, or excess moisture/water may also be performed.

At this stage we should have a rubber crumb suitable for use with the milling portion of the present invention. Rubber crumb (or similar products) from other sources may also be used or added. Small amounts of hydrocarbon rich non-rubber materials may be added though the user will need to optimise for each implemented embodiment the quantity and nature of any other materials which are included. For instance, a small percentage of certain plastics (typically also shredded or in small pieces) may be combined with the rubber crumb.

While different shear mills are known, the preferred milling apparatus is that which is commonly referred to as a hydrafiner within the pulp and paper industry. This is milling apparatus acting primarily as a shear mill which acts on cellulose fibre in wood particles to produce a pulp. It acts as a wet milling process and typically allows fluid to be introduced into the mill through a separate (often independently controllable) feed than the particulate material. When used with rubber crumb and a designated extractant, experiments have indicated that a very fine particle size for the rubber material can be quickly achieved. The currently preferred output size is that of reduced fines (as herein defined). The resultant output is a slurry (current thought to comprise the designated extractant, extracted compounds from the rubber material, and non-dissolved rubber particles. Early experiments suggest an approximate 50:50 (by volume) ratio of extractant to rubber crumb, which produces what is best described as a slurry of gel-like viscosity. In practice an operator can vary these ratios to suit the apparatus being used (e.g. a less viscous slurry might be preferred for instance). The nature of the rubber material can also have a bearing on viscosity, as well the particle size the mill is set to produce. Most embodiments will employ a solvent:rubber ratio of 1:1 to 5:1 and more typically around 2:1 to 4:1 though this will typically be optimised to the particular apparatus, tyre/rubber type or source, extractant type, and optimising the recovery portion of the process. Solvent to rubber ratios outside of the above range are envisaged.

The hydrafiner can be set to process material quite quickly. Wet milling apparatus with a shearing action, such as used for mechanical pulping in the pulp and paper industry, are required to quickly process large volumes of materials and are typically suitable. Other types of shearing mixers, such as in-line shearing mixers, can be considered providing they are designed to accommodate the size of the rubber crumb being introduced and the extractant being used. The result is the rapid processing of rubber crumb to a slurry product ready for the removal of volatiles. This wet shear milling step may be set to be run as a batch process or as a continuous process, according to the design of the milling apparatus and remainder of the plant.

A wide range of wet milling equipment exists, particularly for use in the food and pulp (paper) industries. Such apparatus are sometimes referred to as hydrafiners, or in-line shearing mixers, and mechanical (as well as thermomechanical (TMP)) mills. Each are typically characterised by providing a shearing force to the solid material in a wet environment. While the exact mechanism is not known, it appears that the application of shearing forces to the rubber solid material, in the presence of an extractant, facilitates the release of useful volatile and semi-volatile components from the rubber material and allows for an inline or continuous process to be achieved (c.f. Dobozy). In a preferred embodiment, the rubber is reduced to a particle size typically around 30 to 50 μm, and thus it is desirable that the milling equipment is able to perform this.

In trials by the inventor a single disc refiner comprising two patterned discs (one rotating and one stationary) was used.

As opposed to Dobozy in US5316224, the rubber material is subjected to shearing forces in the presence of solvent. This is a contrast to the presoftening and absorption (of solvent into the rubber) step of Dobozy in which the solid impregnated rubber is removed from solvent and subsequently subjected to shearing forces. However, a consideration of Dobozy is to soften the rubber so that it is more easily removed from any steel reinforcing (see Best Mode of Performing the Invention) and to recover elastomeric rubber material for recycling.

Subsequently the slurry product can be moved to elsewhere in the apparatus, for an inline process, where it can be subjected to one or more distillation steps. In a preferred embodiment two consecutive distillation steps are performed. Initially, in the first phase/step, the slurry may be heated to mild temperature usually not exceeding 130°C (though higher temperatures (typically not exceeding 190°C) may be used). This tends to remove most of the designated extractant components (depending on the extractant used) and volatile components able to be extracted from the rubber material. This may be recycled to the shearing mill, though may be "cleaned up" prior to reintroduction – e.g. further filtering, separation, distillation. This slurry heating step may be performed under reduced pressure.

In the second optional phase/step the pressure is typically reduced to full or partial vacuum. Typically 50 Torr or less is used, though can be varied and optimised by a user. The temperature may be elevated more, reduced, or remain the same depending on the particular embodiment, raw materials, extractants, distillates being recovered, etc. Various temperature and/or pressure profiles may be applied during any heating/distillation steps of the slurry. This second step may represent a second distillation process within the same part of the process apparatus, though often represents a further step down the process line to allow for more continuous processing of the materials. Distillation techniques from within the petrochemical industry may be drawn upon.

Typically the distillation steps yield a residue fraction which can optionally be heated further (typically in excess of 200°C and commonly around 230-250°C). The period and/or temperature profile will typically be until no further significant amount of volatiles are emitted (these volatiles can be recovered or diverted to an earlier distillation chamber (depending on the design of the plant and apparatus)).

The remaining product is typically a carbon rich product, though final heating stage(s) can affect the nature of this product (e.g. carbon content, whether it is an activated charcoal product, etc.). Reduced atmospheric pressure may also be applied during the final heating stage (which can also reduce possible combustion issues).

The recovery of carbon is dependent upon a number of factors such as the parameters used in a particular embodiment. By way of example, a carbon yield of around 7-15% is typical, with the remainder being recovered distillates (including extractants). The carbon produced is typically equivalent to 'pyrolytic carbon' and may be used in carbon additive or carbon construction industries, including steel manufacture, carbon fibre, carbon coatings, inks, tyre manufacture. It also has application across a range of medical and bio-medical applications and the range of applications in which it can be used is quite extensive.

The process of the invention involves a designated extractant. This typically one or more liquids which may act on the rubber material in different ways. Some of these ways include: softening the rubber, plasticising the rubber, chemically extracting components in the rubber, lubricating the rubber particles in mechanical processes, chemically attacking and degrading the rubber, and dissolving the rubber. There are a range of materials which trials suggest are suitable, and combinations may be used. Most of these components are characterised by having melting points under about 190°C at normal atmospheric pressure, and melting points below about 50°C (see below). While low melting point solids may be used (i.e. mp below 50°C), it is envisaged that these will typically be combined with other components which are liquid at the temperature of the shear milling process if they are not liquid themselves at this temperature. More volatile extractants are typically also more easily recovered in the ensuing distillation/volatiles-recovery steps after milling.

Currently preferred extractants are generally organic in nature and typically comprise compounds and mixtures which can either or both: i) dissolve organic compounds which tend to be insoluble or have low solubilities in water, and ii) can degrade the physical characteristics of polymeric and rubber materials.

In respect of the first preferred characteristic, many organic solvents which are liquid at room temperature are capable of dissolving organic compounds, though some are better than others. Preferred solvents in this area tend to include lower molecular weight ketones such as acetone and MEK (methyl ethyl ketone) for example; primarily straight chain hydrocarbons from about C_4 to C_8; halogenated hydrocarbons such as dichloromethane (DCM), trichloroethane, chlorofluorocarbons, etc.; some aldehydes such as butyraldehyde; various cyclic aromatic compounds such as benzene, xylene, toluene, etc; various cyclic non-aromatic compounds such as cyclohexane, etc.; various aromatic and non-aromatic heterocyclic compounds such as dioxane, furan, tetrahydrofuran (THF), pyridine, thiophene, etc; various esters; and various branched and substituted variants of the foregoing. Please note that this list is illustrative only and not intended to be exhaustive. These extractants tend to be good at extracting soluble components (often non-polymeric organic components, or short chain polymeric fragments) from the rubber material – particularly when present as the rubber material is sheared to a reduced fines size. The inventor currently considers that an explanation for the increased speed and efficacy of the action of extractants in the present process (as compared to Dobozy) is that the mechanical action of shearing in the presence of solvent enhances any chemical dissolution occurring; that the shearing action and small particle size also exposes potentially extractable components more efficiently to extractants present; and that the wet shearing action presumably also helps break long polymeric chains to yield potentially extractable components. The exact mechanisms have not yet been studied, but the above explanations represents the inventors best current explanation explaining the high efficacy and rapidity of the present process.

Regarding the second preferred characteristic, some solvents tend to degrade polymeric materials such as rubber. Normally such degradation is relatively slow (hence Dobozy's long period of pre-soaking) and even for Dobozy, the degree of degradation when measured over hours may only be sufficient to soften the rubbers. However introducing these extractants during a wet shearing process appears to often accelerate any degradation action, which may be due to at least either or both of the mechanical action of shearing, and the reduced fines size of the particles. The resulting small size of the particles presents a much larger surface area on which extractants may act and thus the extractants can be more effectively than merely affecting the surface layers of bulk (large) sized particles (e.g. rubber shreds vs. reduced fines).

The type of extractants which can degrade rubber polymers tends to vary according to the specific composition of the rubber, which for tyres can vary considerably. Hence not all compounds and mixtures may effectively degrade all rubbers, and some user optimisation may be required. However, some examples of extractants which can be generally regarded as potentially degrading rubbers include: methanol, lower molecular weight ketones, lower molecular weight halocarbons such as dichloromethane, pine oils, pine and plant oil constituents such as pinene, limonene, and various liquid terpenoids, some tall oils (including tall oil esters), and wood and mineral turpentines. Again, this list is intended to be illustrative rather than exhaustive, and also varies according to the exact nature of the rubber material being used as a raw product.

There are therefore a number of potential different compounds and formulations which may be used as designated extractants, which provides the user with a wide scope for optimising extractants for their particular installation (and operational parameters), safety, economy, and for the particular types of rubber materials being processed.

Typically, for ease, we have classified possible extractants into three main groups which are defined as follows, and wherein a designated extractant may comprise one or more members from one or more of these groups.

The first group is categorised preferred hydrocarbon extractants and comprises: halocarbons, halogenated hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons, substituted cyclic hydrocarbons, substituted aromatic hydrocarbons, cyclohexane, dichoromethane, trichloroethane, xylene, benzene, hexane, heptane, pentane, light naphthas and petroleum distillates, mineral turpentines, kerosenes; all having a boiling point of less than 190°C, and a melting point of less than 50°C at standard atmospheric pressure.

The second group is categorised preferred organic extractants and comprises: ethers, ketones, aldehydes, diethyl ether, acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), butyraldehyde, aromatic and non-aromatic heterocylic compounds with rings comprising carbon and oxygen, dioxane, furan, tetrahydrofuran (THF), aromatic and non-aromatic heterocylic compounds with rings comprising carbon and nitrogen, pyridine, aromatic and non-aromatic heterocylic compounds with rings comprising carbon and sulfur, thiophene, alcohols, methanol; all having a boiling point of less than 250°C, and a melting point of less than 50°C at standard atmospheric pressure.

The third group is categorised preferred plant based extractants and comprises: light vegetable oils, wood turpentines, wood alcohols, terpenes, pine oils, tall oils, oils extracted from wood, oils extracted from seeds, terpenoids, pinene, limonene, all having a boiling point of less than 250°C, and a melting point of less than 50°C at standard atmospheric pressure.

The choice extractant can be influenced by a number of factors – e.g. cost, characteristics of the rubber material, aggressiveness towards the rubber, aggressiveness towards processing apparatus, nature of the obtained distillate fractions, etc. In relation to the last factor, some embodiments of the present invention may be used to produced a fuel or a particular petroleum type fraction, rather than isolating components into relatively pure fractions. When fuels or fractions are all that are desired, then the choice of extractant can have a bearing of the quality of the product. For instance, when producing a fuel, an extractant such as MEK (methyl ethyl ketone) may be very efficient, but too expensive (and too volatile) to remain in a distillate fraction intended for use as a fuel. In such a case, when producing a diesel fuel (for instance) it may be desirable to use a lower price extractant comprising turpentine or a light grade kerosene for example. The resulting fuel product will be the combination of the extractant with extracted components from the rubber. Here, the user is provided with a great degree of choice to optimise the process, by suitable selection of raw materials, to tailor the product obtained from the process.

By way of example of a preferred embodiment: the first distillation recovery typically yields what is known in the industry as a kerosene product. The second recovered distillate is what is known as a diesel product (light oil). By reintroducing the diesel product back into the crumb slurry a jet fuel can be produced in the first distillate fraction.

The present invention will now be further described in relation to some specific illustrative examples.

DESCRIPTION OF PREFERRED EMBODIMENTS

Example 1 – Preliminary optional steps for producing rubber crumb

A bulk material comprising predominantly used tyres may be cleaned and washed to remove foreign materials and contaminants.

The bulk material is then shredded to provide rubber shreds which are nominally within the range of 40mm to 75mm (inclusive) particle size. The shreds may be screened to remove larger particles which can be returned for re-shredding.

The shreds may be optionally dried to remove any excess moisture or water which may be present (though drying may take place earlier or later in the process of preparing a rubber crumb). Waste heat from subsequent distillation processes may be used for drying.

The shreds are then introduced to a hammer mill capable of reducing the size of the rubber material to a nominal size of 5mm to 10mm (inclusive) average particle size. Steel from belted tyres may be present in the output. The crumb output may be screened, and/or use various separation techniques (e.g. magnetic separation) to remove contaminants and metal which are present. The result is ideally a rubber crumb of the above mentioned nominal size and which is relatively free on non-organic compounds and materials.

Example 2 – Preparation of carbon rich product from rubber crumb

A rubber crumb is chosen as the raw material, ideally such as produced in example 1. A small proportion (i.e. less than or equal to 25%) of other polymeric materials (e.g. plastics) may be included.

The dry crumb is introduced into a wet shearing mill such as a hydrafiner as used in the pulp and paper industry (though this may need to be modified to ensure any seals and fittings are not affected by the designated extractant, and reduce flammability or explosion issues – such modifications would be within the skill of a suitably qualified tradesperson dealing with flammable hazardous plant).

A designated extractant is introduced into the hydrafiner to maintain an approximate ratio (by volume to rubber crumb to designated extractant) within the inclusive range 20:80 to 65:35, and ideally around 50:50. Specific embodiments may be chosen to operate outside of this preferred range according to user preference.

Designated extractants for this example may comprise one or more of the following formulations:

Formulation A: wood or mineral turpentine.

Formulation B: a mixture of wood or mineral turpentine; pine oil, and optionally tall oil.

Formulation B: low molecular weight aggressive solvents (e.g. dichloromethane, methylethyl ketone (MEK)) , with hydrocarbons (e.g. C4-C10 hydrocarbons, lower boiling point kerosenes, light naphthas (boiling nominally between 60°C and 190°C at atmospheric pressure).

The shearing mill is set up to produce a rubber particle of average nominal size of $1\mu m$ to $100\mu m$ (inclusive). In one preferred embodiment he preference is around $40\mu m$. Nominally also the average time to reduce the rubber crumb to reduced fines of the above size should be set to be less than 10 minutes, with ideal processing rates (depending on the equipment) being less than 1 minute.

The output should be a slurry of reduced fines dispersed in extractant. At a 50:50 volume ratio (rubber crumb to designated extractant) the slurry is of a gel like consistency. A higher proportion of extractant can be used, but this also means more solvent to recover.

The next step(s) involve the recovery of volatiles. Mechanical separation steps (e.g. filtration (preferably under pressure), centrifuging, etc.) may optionally be performed to remove bulk extractant from the mixture. However consideration needs to also be given that this could reduce the total amount of volatiles recovered from the slurry as the extractants may also have a tendency to potentially draw out further volatiles entrapped in the rubber fines in the slurry. Hence, some optimisation for a given installation should be performed to test the economics of mechanical separation processes supplementing distillation and heating.

Assuming (for this example) there to be no prior mechanical separation, the slurry would be pumped to a suitable heating chamber which may comprise a heat pipe through which the slurry flows (there may be a temperature gradient along this pipe). Alternatively the slurry may be pumped (e.g. a screw conveyor or fluid pump) to a suitable chamber.

In this example, the slurry is initially heated to around 105°C to 120°C for the formulations given. The volatiles which boil off are collected, and may be collected as different fractions depending on their intended end use. Various fractional distillation techniques as used in the petrochemical industry may be employed according to user needs. In the present example a cracking column (such as used in the petrochemical industry) is used).

In this example the slurry is subjected to a second heating stage in which the pressure is reduced (ideally to 50 Torr or less (this will also be governed partly by the volume of volatiles still coming off) and finishing at a pressure of 5 Torr or less once the majority of volatiles have been distilled). The temperature may optionally be increased to around 150°C to 180°C to drive off more stubborn volatiles. At this stage we should be left with a substantially dry residue fraction.

Once the bulk of volatiles have been distilled, the slurry temperature is raised to 260°C or higher, and preferably around 380-410°C. There may be a few more volatiles which are driven off at this stage, including break down products as the remaining residue fraction converts primarily to carbon. The heating temperature and time continues until a suitably compositioned carbon rich product is obtained. The heating parameters can be varied to obtain a product whose nature matches the user's requirements, though a charcoal product can be effectively obtained under the correct heating parameters, and which may comprise an activated charcoal product. The product is typically an easy to crumble cake-like residue.

The aforementioned process is amenable to a batch or flow type process, particular due to the elimination of pre-soaking steps and the rapidity of action of the wet shearing stage. It is considered that a skilled reader can suitably design plant and apparatus (based on the description herein) which can implement the process as either a batch, part batch, or continuous flow process. Plant and technologies from the petrochemical industry can be applied in the design of any of these types of plant.

<u>Example 3 – Preparation of carbon rich product and distillates from rubber crumb</u>

A rubber crumb is chosen as the raw material, ideally such as produced in example 1. A small proportion (i.e. less than or equal to 25%) of other polymeric materials (e.g. plastics) may be included.

The dry crumb is introduced into a wet shearing mill such as a hydrafiner as used in the pulp and paper industry (though this may need to be modified to ensure any seals and fittings are not affected by the designated extractant, and reduce flammability or explosion issues – such modifications would be within the skill of a suitably qualified tradesperson dealing with flammable hazardous plant).

A designated extractant comprising wood or mineral turpentine is introduced into the hydrafiner to maintain an approximate ratio (by volume to rubber crumb to designated extractant) within the inclusive range 10:90 to 30:70, and ideally around 20:80. Specific embodiments may be chosen to operate outside of this preferred range according to user preference.

The shearing mill is set up to produce a rubber particle of average nominal size of 1μm to 100μm (inclusive). Nominally also the average time to reduce the rubber crumb to reduced fines of the above size should be set to be less than 10 minutes, with ideal processing rates (depending on the equipment) being less than 1 minute.

The output should be a slurry of reduced fines dispersed in extractant. At a 20:80 volume ratio (rubber crumb to designated extractant) the slurry is of a fluid gel like consistency but again depends on a number of factors. A higher proportion of extractant can be used, but this also means more solvent to recover.

The next step(s) involve the recovery of volatiles. Mechanical separation steps (e.g. filtration (preferably under pressure), centrifuging, etc.) may optionally be performed to remove bulk extractant from the mixture. However consideration needs to also be given that this could reduce the total amount of volatiles recovered from the slurry as the extractants may also have a tendency to potentially draw out further volatiles entrapped in the rubber fines in the slurry. Hence, some optimisation for a given installation should be performed to test the economics of mechanical separation processes supplementing distillation and heating.

Assuming (for this example) there to be no prior mechanical separation, the slurry would be pumped to a suitable heating chamber which may comprise a heat pipe through which the slurry flows (there may be a temperature gradient along this pipe). Alternatively the slurry may be pumped (e.g. a screw conveyor or fluid pump) to a suitable chamber.

In this example, the slurry is initially heated to around 140 to 160°. The volatiles which boil off are collected, and may be collected as different fractions depending on their intended end use. However, the majority of recovered distillate at this temperature will be turpentine, which can be recycled either with, or without, further purification or refinement by distillation. This step can be performed in a rotary kiln, though other heating equipment suitable for dealing with slurries may be used.

The resultant mass is then subjected to a second heating stage in which the pressure is optionally reduced (ideally to 50Torr or less (this will also be governed partly by the volume of volatiles still coming off) and finishing at a pressure of 5 Torr or less once the majority of volatiles have been distilled). The temperature may optionally be increased to around 160°C to 240°C to drive off more stubborn volatiles, and higher if a reduced pressure is not used. At this stage we should be left with a substantially dry residue fraction. This stage is ideally conducted in a rotary kiln. The temperature may be progressively increased, and/or any pressure reduction progressively increased, so that different distillate fractions can be recovered. Typically trial experiments have shown that kerosene, and light diesel fractions are obtained (apart from any remaining original solvent (turpentine)).

Once the bulk of volatiles have been distilled, the slurry temperature is optionally raised to 260°C or higher (e.g. 300-400°C). There may be a few more volatiles which are driven off at this stage, including break down products as the remaining residue fraction converts primarily to carbon. The heating temperature and time continues until a suitably compositioned carbon rich product is obtained. The heating parameters can be varied to obtain a product whose nature matches the user's requirements, though a charcoal product can be effectively obtained under the correct heating parameters, and which may comprise an activated charcoal product. The product is typically an easy to crumble cake-like residue.

The aforementioned process is amenable to a batch or flow type process, particular due to the elimination of pre-soaking steps and the rapidity of action of the wet shearing stage. It is considered that a skilled reader can suitably design plant and apparatus (based on the description herein) which can implement the process as either a batch, part batch, or continuous flow process. Plant and technologies from the petrochemical industry can be applied in the design of any of these types of plant.

Example 3 – Preparation of distillate products from rubber crumb

Rubber crumb of average size 5mm was introduced into a hydrafiner (wet mill) with one or more of the following solvents: Methyl Ethyl Ketone (MEK) A, Toluene B, Turpentine C.

The ratio of solvent to rubber was maintained approximately within the range of 1:3 (solid to liquid) to produce a slurry. The average particle size of rubber particles in the slurry was approximately within the range of 20 to 100 micrometres.

The slurry had the consistency of a pulpable liquid.

The slurry was then subjected to the following steps:

It was initially heated in a heat exchanger to a temperature approximately within a range of 135 to 180C. The volatiles, which typically comprise solvent, isoprene, kerosene, jet fuel, petrol and reflux are collected and these are used as fuel alternatives or for reprocessing through the system to effect different fuel alternative outcomes. The jet fuel obtained typically has a low sulphur content (typically <0.03% though the nature of the rubber can have a bearing on this) which puts it in the range for jet A fuel without further distillation or purification to reduce sulphur levels.

Of note, the parameters of the process can be set up to obtain kerosene, jet fuel, and diesel fuel products which do not require further refining or blending – which from a manufacturing and cost perspective, is quite significant.

The remaining slurry is then introduced to a rotary kiln where further heating and extraction of volatiles occurs leaving a dry carbon powder. (equivalent to a Pyrolytic carbon)

This additional heating is at around 300 – 400°C and yields further fuel alternatives such as diesel, light oil.

Some notes and observations by the inventor are given by way of example only in terms of helping to understand the invention. They are not intended to be limiting.

M.E.K (Methyl Ethyl Ketone also known as Butanone) produced good results in terms of crumb absorption and fuel output and quality but suffers potential issues health hazards and cost.

Toluene produced good results in terms of crumb absorption and fuel output and quality but currently is not cost effective unless recovered. The use of cheaper less pure forms of toluene could be considered.

Kerosene produced poor results in terms of fuel output and quality and tended to produce a product with an incorrect flash point for use in a preferred fuel product, but this may not be a problem for products with other uses.

Plant derived Turpentine produced excellent results but currently has major drawbacks in terms of availability and cost otherwise would be very suitable for fuel type products.

Mineral Turpentine has thus far produced the overall best results in terms of fuel output and quality along with cost and manageability

The turpentines have had the least affect on plastic components or piping. Others dissolved some of these components over time.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the spirit or scope of the present invention as described herein.

It should also be understood that the term “comprise” where used herein is not to be considered to be used in a limiting sense. Accordingly, ‘comprise’ does not represent nor define an exclusive set of items, but includes the possibility of other components and items being added to the list.

This specification is also based on the understanding of the inventor regarding the prior art. The prior art description should not be regarded as being authoritative disclosure on the true state of the prior art but rather as referencing considerations brought to the mind and attention of the inventor when developing this invention.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the spirit or scope of the present invention as described herein.

It should also be understood that the term “comprise” where used herein is not to be considered to be used in a limiting sense. Accordingly, ‘comprise’ does not represent nor define an exclusive set of items, but includes the possibility of other components and items being added to the list.

This specification is also based on the understanding of the inventor regarding the prior art. The prior art description should not be regarded as being authoritative disclosure on the true state of the prior art but rather as referencing considerations brought to the mind and attention of the inventor when developing this invention.

THE CLAIMS DEFINING THE INVENTION ARE:

1. A method for recycling rubber materials comprising steps of:
    i) introducing rubber crumb into a shearing mill capable of a wet milling process;
    ii) introducing at least one designated extractant to said rubber material so that milling occurs in the presence of said designated extractant;
    iii) milling the rubber material to the size of reduced fines, as herein defined, to create a rubber slurry with said designated extractant;
    iv) subjecting the rubber slurry to a heating stage to remove distillate fractions.

2. A method for recycling rubber materials as claimed in claim 1 comprising the additional step of:
    v) subjecting the residue fraction of step (iv) to a heating stage to create a substantially dry carbon rich product.

3. A method for recycling rubber materials as claimed in claim 1 or claim 2 which includes a preliminary step of producing rubber crumb from shredded rubber by a milling process which includes a non-shearing action.

4. A method for recycling rubber materials as claimed in claim 3 in which the non-shearing milling process comprises a hammering or impacting action.

5. A method for recycling rubber materials as claimed in claim 3 or claim 4 in which the non-shearing milling process is optimised to separate non-rubber materials embedded in, or attached to, the shredded rubber from the rubber materials therein.

6. A method for recycling rubber materials as claimed in any one of the preceding claims in which there is an additional step of separating non-rubber materials from the rubber crumb produced.

7. A method for recycling rubber materials as claimed in claim 6 in which the separation process is a magnetic separation process.

8. A method for recycling rubber materials as claimed in any one of the preceding claims in which there is included a drying step to remove water and moisture from the rubber crumb before it is subjected to a wet milling process.

9. A method for recycling rubber materials as claimed in any one of the preceding claims in which the designated extractant is added to said rubber crumb once it is in the shearing mill.

10. A method for recycling rubber materials as claimed in any one of the preceding claims in which the designated extractant is selected to also act as a lubricant to rubber crumb being milled in the shearing mill.

11. A method for recycling rubber materials as claimed in any one of the preceding claims in which the designated extractant comprises one or more members of any one or more subgroups in the group comprising: preferred hydrocarbon extracts, preferred organic extractants, and preferred plant based extractants.

12. A method for recycling rubber materials as claimed in claim 11 in which the group of preferred hydrocarbon extractants comprises: halocarbons, halogenated hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons, substituted cyclic hydrocarbons, substituted aromatic hydrocarbons, cyclohexane, dichoromethane, trichloroethane, xylene, benzene, hexane, heptane, pentane, light naphthas and petroleum distillates, mineral turpentines, kerosenes; all having a boiling point of less than 190°C, and a melting point of less than 50°C at standard atmospheric pressure.

13. A method for recycling rubber materials as claimed in claim 11 in which the group of preferred organic extractants comprises: ethers, ketones, aldehydes, diethyl ether, acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), butyraldehyde, aromatic and non-aromatic heterocylic compounds with rings comprising carbon and oxygen, dioxane, furan, tetrahydrofuran (THF), aromatic and non-aromatic heterocylic compounds with rings comprising carbon and nitrogen, pyridine, aromatic and non-aromatic heterocylic compounds with rings comprising carbon and sulfur, thiophene, alcohols, methanol; all having a

boiling point of less than 250°C, and a melting point of less than 50°C at standard atmospheric pressure.

14. A method for recycling rubber materials as claimed in claim 11 in which the group of preferred plant based extractants comprises: light vegetable oils, wood turpentines, wood alcohols, terpenes, pine oils, tall oils, oils extracted from wood, oils extracted from seeds, terpenoids, pinene, limonene, all having a boiling point of less than 250°C, and a melting point of less than 50°C at standard atmospheric pressure.

15. A method for recycling rubber materials as claimed in any one of the preceding claims in which prior to heating of the rubber slurry there is at least one mechanical separation step to separate liquid from solid components.

16. A method for recycling rubber materials as claimed in claim 15 in which a said mechanical separation step comprises one or more of: decanting, centrifuging, filtration, and fluid absorption into a medium from which it can be recovered.

17. A method for recycling rubber materials as claimed in claim 15 in which the mechanical separation step comprises a pressurised filtration method.

18. A method for recycling rubber materials as claimed in any one of the preceding claims in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a temperature of 190°C or less.

19. A method for recycling rubber materials as claimed in any one of the preceding claims in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a temperature of 140°C or less.

20. A method for recycling rubber materials as claimed in any one of the preceding claims in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a reduced pressure, which is less than atmospheric pressure.

21. A method for recycling rubber materials as claimed in claim 20 in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a reduced pressure of 50 Torr or less.

22. A method for recycling rubber materials as claimed in claim 20 in which heating of the rubber slurry to remove distillate fractions comprises a step which occurs at a reduced pressure of 5 Torr or less.

23. A method for recycling rubber materials as claimed in any one of the preceding claims in which at least part of said distillate fractions are reintroduced as designated extractant into the shearing mill.

24. A method for recycling rubber materials as claimed in claim 23 in which said reintroduced distillate fractions comprise mainly recovered designated extractant from the rubber slurry.

25. A method for recycling rubber materials as claimed in claim 2, or in any one of claims 3 through 24 when dependent on claim 2, in which heating of the residue fraction occurs at a temperature exceeding 200°C.

26. A method for recycling rubber materials as claimed in claim 2, or in any one of claims 3 through 24 when dependent on claim 2, in which heating of the residue fraction occurs at a temperature exceeding 350°C.

27. A method for recycling rubber materials as claimed in claim 2, or in any one of claims 3 through 26 when dependent on claim 2, in which heating of the residue fraction occurs, for at least part of the time, at a reduced pressure.

28. A method for recycling rubber materials as claimed in claim 2, or in any one of claims 3 through 26 when dependent on claim 2, in which, when heating of the residue fraction occurs, distilled volatiles are collected.

29. A method for recycling rubber materials as claimed in claim 28, in which distilled volatiles are reintroduced to the rubber slurry and or distillate fractions occurring prior to the heating of the residue fraction.

30. A method for recycling rubber materials as claimed in any one of the preceding claims in which the method is performed as a sequence of batch steps.

31. A method for recycling rubber materials as claimed in any one of claims 1 through 29, in which the method is performed substantially as a continuous process.

32. Apparatus for performing a method as claimed in any one of the preceding claims, said apparatus comprising a shearing mill capable of wet processing of rubber crumb in the presence of an extractant, delivery means for rubber slurry produced by the shearing mill to a heating chamber, heating means for elevating the temperature of rubber slurry within the chamber, and distillation apparatus for recovering volatiles

33. Apparatus as claimed in claim 32, in which the same heating chamber is used for heating the slurry and residue fractions.

34. A carbon rich solid product, obtained from the processing of rubber according to a method as claimed in any one of claims 1 through 31.

35. A distilled product obtained from performing the method of any one of claims 1 through 31.

36. A method for the processing of rubber, substantially as described herein with reference to the contained examples.