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PROCESS OF MAKING THERMOPLASTIC COMPOSITIONS CONTAINING RUBBER AND THE LIKE

Edward R. Dillehay, Glen Ellyn, Ill., assignor to The Richardson Company, Lockland, Ohio, a corporation of Ohio

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This application is a continuation in part of my copending application Serial No. 562,426 filed September 11, 1931, and entitled Asphaltic storage battery cases.

My invention relates to the manufacture of asphaltic storage battery cases which, as regularly made, are formed of a composition of bitumen, preferably an asphaltic blend high in gilsonite, or blown asphaltic substances having equivalent characteristics to such blend, and acid resistant mineral filler, fibrous or not as desired, and vegetable fibers in an amount preferably not greater than 15%, the said composition being molded under great pressure in suitable dies. The characteristics of such battery boxes and the functions of the several ingredients therein are known in the art, and need not be specially outlined by me. Reference may be made to Patent No. 1,752,917 to A. R. Lukens.

It is sufficient to point out that in bituminous binders hardness is usually accompanied by a degree of brittleness, and tends to vary inversely to toughness and resistance to shatter. Hardness in the bitumen at ordinary temperatures makes for stiffness in the box and resistance to distortion at higher temperatures, but is somewhat opposed to the toughness and elasticity which make for resistance to cracking at low temperatures. Different bitumens exhibit different combinations of these qualities, as well as softening points and breadth of plastic ranges between liquid stages and solid stages. It has been the practice in the art in the known way to select and/or blend bitumens to secure an optimum mean between relatively opposed characteristics; and in general, blends of tough, blown asphalts with gilsonite have been found most suitable. Some bituminous substances are capable of being blown to give binders of suitable hardness without sacrifice of toughness and others are capable of being separated into constituents which are likewise suitable to give binders of the desired type without the use of gilsonite. Filler materials have a primary hardening function, though they contribute measurably to tensile strength even when non-fibrous. Fibrous materials contribute primarily to toughness and tensile strength.

For simplicity in disclosure, my invention may be thought of as applied to asphaltic battery boxes and compounds therefor of the general type which I have mentioned, although the practice of my invention enables me to make certain departures from elements which have heretofore been considered fixed. The primary object of my invention is the attainment of enhanced properties in articles and molding compositions of the character to which my invention is addressed, without the sacrifice of other useful qualities. More particularly it is an object of my invention to enhance the desirable qualities of the binder materials employed, and to achieve great toughness, tensile strength, and resistance to crack and shatter, without at the same time sacrificing high temperature resistance.

These and other objects of my invention which will be pointed out hereinafter or will be apparent to one skilled in the art upon reading these specifications, I accomplish in that composition and by those certain processes of which I shall hereinafter describe certain preferred embodiments.

Preferably in the practice of my invention I secure enhanced qualities in the binders of plastic compositions, of which the main binder ingredient is bitumen, by the addition thereto of certain relatively smaller quantities of rubber or equivalent gums. Battery boxes have hitherto been made of vulcanized rubber, but it is not to these that my invention is addressed. Both new and reclaimed rubbers have been used in vulcanized battery boxes, and it is common to add to the rubber itself bituminous materials as a diluent. Such bituminous substances have usually been referred to as mineral rubbers, and they have been added to and compounded into rubber compositions by the usual rubber technique in amounts up to 34%, or even somewhat greater. The rubber battery box however has problems, characteristics, and a technique which are peculiar to it, and with which my invention is not concerned. In particular the final characteristics of such boxes are determined by vulcanization with sulphur under heat and pressure.

I have discovered however that certain very desirable qualities may be built up in an asphaltic or other bituminous binder and in an unvulcanized article, by the addition thereto of certain relatively small percentages of rubber without sacrificing other peculiar and desirable qualities of the bituminous binder and without stepping over into the rubber box technique. I have found it possible in unvulcanized articles to secure a very considerable increase in resistance to temperature change, and to shatter, crack and deflection, without the making of the ultimate mix upon rubber grinding rolls or mixing rolls, and by following the usual technique employed in the manufacture of unvulcanized articles having a thermoplastic binder, such as asphaltic storage battery cases, with the addition of a quantity of rubber or a blend of rubber and bitumen, as will hereinafter be more fully set forth. I thus am able to make molded articles, of which battery boxes are an example, by mixing the composition in a Werner-Pfleiderer or other mixer, with substantially the same time cycle and under the same commercial conditions as have been practiced hitherto in the asphaltic battery box or analogous art. I am thus not limited to a

mixing of the complete composition upon grinding rolls or other mixing and grinding machinery, which changes the character thereof and which results in some instances in a type of fiber condition which would be unsatisfactory for the purposes and under the conditions involved in the manufacture of asphaltic storage battery cases. It will be understood that in rubber manufacture not only is there a tendency for the rolls to grind up vegetable fibers and other filler materials incorporated into the batch, but also that the main strength of the composition comes from the final character of the vulcanized rubber itself. Filler materials in rubber compositions are thus in the nature of diluents having some hardening function, and rubber battery boxes do not in general exhibit the characteristics of boxes having an unvulcanized, thermo-plastic binder substance containing a filler and fibers. The differences between the rubber technique and the asphalt technique have therefore never been bridged by any intermediate procedure.

Essentially in the practice of my invention I have found that marked improvements may be made in bituminous, thermo-plastic binders, by the addition thereto of rubber or equivalent gums, providing the rubber and bitumen are so mixed together as to give a substantially homogeneous combined binder substance. In the addition of rubber or the like to a bitumen to give the results which I secure in a thermo-plastic unvulcanized binder, the main problems are twofold. In the first place the rubber or equivalent substances must be mixed with a bituminous binder so as to give in substantial part at least, the homogeneous result referred to; and in the second place the rubber should not be broken down, for the purpose of incorporating it or during the incorporation steps, to such an extent as will vitiate the desired results.

I have secured excellent and comparative results with a number of different types of rubber, for example, including, but without limitation, crude or new rubbers, reclaimed rubbers, which may or may not have been devulcanized, and vulcanized rubbers. By vulcanized rubbers I mean rubbers which have been vulcanized with less than the greatest quantity of sulphur which they will absorb, as distinguished from hard rubbers which have utility primarily as filler materials only. An available source of vulcanized rubber is the so-called tire peel which comprises the outer portions of used automobile tires and does not contain as much fibrous material as the reclaimed rubbers frequently contain. I may also employ rubbers which have been softened by solvent action or have even been reduced to a liquid by solvent action. I also may employ rubber dispersions including natural latex and artificial rubber dispersions.

The quantity of rubber employed as compared with the bituminous or thermoplastic binder may vary within quite wide limits. I have secured excellent results with quantities of rubber ranging from 2 to 3% of the total weight of the mix including fillers and fibre up to 25 to 35% and even therebeyond. Different quantities of rubber may be used in different compositions for securing different effects. In a battery box composition for example the endeavor will be to use only so much of the rubber as is necessary to secure the desired toughening action and resistance to shatter and temperature change, inasmuch as the rubber is a more expensive ingredient than the bitumen. I ordinarily prefer to employ in asphaltic battery boxes rubber to the extent of 8 or 8½% of the total mix. The quantity of rubber as well as the particular kinds and sources of the rubber or equivalent gum may largely be determined by considerations of economy.

When dealing with rubber in a fluid or semi-fluid and thinly plastic condition, it may be mixed with the other ingredients of the box or molded article in the ordinary processes of manufacture thereof and at substantially any stage inasmuch as no great intensity of mechanical action will be necessary to give a homogeneous result. The amount of mechanical work necessary to produce a homogeneous binder may be employed to govern the stage of the process at which the rubber is added, especially since the amount of mechanical work on the rubber itself should be kept as low as possible to avoid any more breaking down of the rubber than is necessary to secure complete incorporation. Thus rubber solutions or dispersions may be incorporated if desired, into the mix as a final operation in the ordinary mixing and after the substantially complete incorporation of the other ingredients. The heat of the mixer will drive off the water in the case of dispersions and the solvent in the case of solutions; and the solvent may if desired be recovered in any known way.

Example #1

I make a battery box to the following exemplary formula:

	Per cent
Hard bitumen	43
Diatomaceous earth (siliceous)	38
Cotton linters	11
Rubber hydrocarbon	8

When using dispersions or solutions of rubber the rubber may be calculated upon the actual hydrocarbon content thereof and appropriate quantities of the dispersion or solution used.

My usual practice will be to first thoroughly blend the bitumen and filler in a Werner-Pfleiderer or similar mixing machine under heat, and afterward add and incorporate the fibre. The rubber may be added after the completion of the rest of the mix, or before. In either event there will be sufficient subsequent mixing to blend the rubber with the bitumen, but it is advantageous when working with rubber in these forms to add it at a late stage in the mixing to avoid excessive breaking down action. The dispersing medium or the solvent will of course be driven off by the heat of the mixing operation.

A relatively soft type of rubber material which may be employed is reclaimed rubber available commercially. Reclaimed rubber is ordinarily made from old tires, boots and other rubber articles and contains considerable fiber. The rubber after comminuting is cooked with caustic. Some reclaimed rubber is termed high cellulose reclaim. This material has had a shorter cooking with less caustic; and the cellulose in it, which ordinarily runs in the neighborhood of 10 to 15%, is mostly in a charred condition. This material may be used, but it does not give a high finish result inasmuch as the surface of the resultant molded compound is inclined to be rough and pitted. For many uses however this is not a disadvantage.

The so-called low cellulose reclaim is a used rubber which has been subjected to a longer cooking operation with stronger caustic, and is slightly more expensive. In it, the fiber no

longer exists as such. It is somewhat more advantageous to use this material because it goes in more smoothly and gives a result capable of taking a higher finish.

In the use of reclaimed rubbers I ordinarily take a suitable binder of hard asphalt with or without gilsonite as indicated, and mix therewith in a suitable mixer such as a Werner-Pfleiderer or Banbury mixer the filler materials which I propose to use. After the incorporation of the filler I throw in the reclaimed rubber and continue the mixing until the rubber is thoroughly dispersed. If the reclaimed rubber is initially too hard for ready dispersion it may be given one or two passes on the rubber rolls for the purpose of breaking it down slightly; but this will not ordinarily be necessary. With the relatively soft types of reclaim available a very few minutes of mixing will usually be sufficient to give a homogeneous result, since the rubber readily amalgamates with the asphalt. I prefer to mix the filler (which in this instance will usually be a siliceous ditomaceous earth or a pyrax talc) with the bitumen first because this not only shortens the time of mixing, so far as the rubber is concerned, but also assists in securing an even dispersion of the rubber. After the dispersion of rubber I then add my fiber and mix it until it is incorporated, usually from 10 to 15 minutes.

Example #2

I may make a case using reclaim to the following exemplary formula:

	Per cent
Hard alphalt	39
Pyrax talc	40
Cotton linters	11
Reclaimed rubber	10

by the method set forth. Reclaimed rubber usually contains only about 50 to 60% rubber hydrocarbon, and as a result the above formula gives about 5% or 6% actual rubber.

The effect of rubber so far as the actual mixing is concerned is measurably to stiffen up the mix so that it is not ordinarily necessary to add water during the mixing operation, although this may be done if desired. After the mix has been made as described it may, if desired, be run through a Watson mixer and severed into convenient molding units.

As I have indicated, precaution should be taken not to break down the rubber any more than is necessary in order to secure a homogeneous binder result, for the reason that the more the rubber is broken down the less advantageous will be the strengthening effect thereof. Rubber may be broken down both by intense mechanical action or by heat or by a combination of the two. When working with harder forms of rubber substances it is preferable to soften them by ways which I shall hereinafter set forth; but results may be secured by mixing such rubbery materials directly with asphalt. If this is attempted the long and intense cycle of mechanical work necessary to give substantial homogeneity will dictate the addition of rubber to the bitumen prior to the addition of other ingredients. Thus it is possible to take the bitumen and the rubber and work them together on the rubber rolls or in a Banbury mixer or its equivalent until substantial homogeneity is obtained afterwards adding the other ingredients under conditions of less intense mechanical action as in a Werner-Pfleiderer type of mixer. Starting with either crude rubber or unreclaimed used rubbers the results of this operation are not preferred, since it is difficult to get complete smoothness and homogeneity although a degree of dispersion which will produce the desirable binder effects may be obtained. Where such hard materials are to be used without pretreatment, I find it advantageous to mix them first with a small quantity of bituminous or other substance to form a blend, afterward using this with a larger quantity of bituminous binder. With softer types of rubber materials excellent results may be secured by forming a blend of these with hard bitumens but where the tougher types are employed I prefer to use relatively light bituminous or the like substances as softening materials and increase the hardness of the main body of the binder in a proportionate way to compensate for this.

In an exemplary practice I may mix 50% or thereabouts of hard blown asphalt such as one having a melting or softening point in the neighborhood of 300° F. with 50% or thereabouts of reclaimed or crude or new or used rubber on the rubber grinding roll. Where using new or crude or used rubbers without previous softening treatment, I prefer however to employ a lighter hydrocarbon substance such as an asphalt having a melting point around 120° F. or other light oils, such as pine tar or pine tar oil, oils derived from coal tar, mineral oil, hardwood tar, wax tailings and the like. I prefer to compound the rubber and the bitumen or the softening oil thoroughly on hot rubber mixing or grinding rolls or in one of the pressure mixers such as the Banbury in which very intense mechanical action may be had.

The exact quantities of materials in this blend may be varied to suit requirements, as may also their individual characteristics. My object in this step is to produce a material, bearing rubber, which may be added as such to the ordinary binder employed in the manufacture of battery boxes or similar articles, or to the mixer in which a battery box composition is being made, without a change in the general technique.

It would doubtless be possible to carry on the entire compounding and mixing operations upon grinding or mixing rolls, including the fabrication of the compound itself, but this, for reasons given hereinabove, is not to be preferred. It should also be pointed out that I add to a bituminous binder a relatively small percentage of rubber, and aside from the other advantages of my procedure as outlined, I find that this relatively small quantity of rubber may be distributed completely and homogeneously in a much larger quantity of asphaltic binder with greater ease and in a much shorter time by the process outlined herein.

In the manufacture of a battery case, I may and ordinarily I do substitute 10% of the blend of rubber and bitumen just described for 10% of the binder. The rubber and asphalt combination blends in very well with the remainder of the binder. It will usually be added to the other binder in the mixer or mixers employed, and it may be added while either or both of the binder increments are liquid or not, as desired. At the same temperatures the addition of my rubber blend to an asphaltic binder gives a measurably stiffer combined binder, and consequently a stiffer composition in the mixing operation. This may increase the time cycle of mixing by a relatively short period; and in some instances the worker may prefer to employ, instead of the ordinary dough mixer device, a mixer having a more in-

tense mechanical action whereby the time cycle may be shorter. This, however, is not necessary and exactly the same technique may be employed with my new composition as has hitherto been employed with asphaltic moulding compositions.

The moulded boxes made of my composition are considerably tougher than battery boxes heretofore made and show a better shatter test and a high pendulum crack, with no sacrifice of the stiffness of the box. As a basis of standard comparison, it may be said that a battery box in which 10% of the regular binder has been displaced by 10% of my rubber blend, will show markedly superior properties as outlined over a battery box containing the standard binder alone. My battery box also stands up markedly better upon the freeze test, that is to say on changes of temperature from a very low temperature to a comparatively high temperature in repeated cycles.

Example #3

As an example of a specific formula (but of course without limitation), I have employed a bituminous binder comprising 35% Stanolite asphalt, 30% gilsonite, and 35% Stanolind asphalt which blended together gives me a binder having a softening point at 240° F., and a penetration of 13 at 150° F. Another exemplary binder formula might comprise 10% Stanolite asphalt (140 melting point), 40% blown petroleum asphalt such as Parolite (160 melting point), 50% gilsonite, which after blending together should be blown with air until a melting point of 275° F. and a penetration of 10 at 150° F. are obtained. I have employed a rubber asphalt blend containing 50% Korite asphalt having a softening point of 314° F. and 50% of reclaimed rubber. I have made a battery box composition employing 48% of the said bituminous binder, 10% of the said asphalt rubber blend, 30% of diatomaceous earth such as celite, and 12% of vegetable fiber such as cotton linters. Representative boxes moulded from this composition have exhibited an average tensile strength of 1025 lbs. per square inch, and considerably enhanced value upon the regular bar shatter, side and end deflection, and pendulum crack tests upon the sides and ends and resistance to temperature changes.

In many instances it will be found preferable to take used rubber stock such as tire peel and after running it through a machine known as a hog so as to cut it into relatively small pieces, refine it, i. e. reduce it to a granular form by running it through heavy rolls set tight. The granular material, which may contain some fiber from the breaker strip in the tire, may then be placed in pans together with a portion of softening substance such as pine tar, pine tar oil, light petroleum asphalt, wax tailings, various oils derived from coal tar, various oils derived from hard wood, mineral oil and the like. The material may then be subjected to direct steam pressure sufficient to produce considerable heat therein. The heat may vary with the time of cooking and other factors, and may in some instances run up to 375° F. The material is treated in this way without agitation until it is softened. When softened it will still be in a granular condition ordinarily, but will go together readily if given a number of passes through the rubber rolls. Moreover its viscosity will be such as to produce a breaking up of any fibrous masses therein upon a relatively short treatment, and the softened rubber substance may thereupon be employed as I have hereinabove indicated for reclaimed rubber.

Example #4

Refined tire peel in the amount of say, 900 pounds is mixed with 100 pounds soft petroleum asphalt having a melting point around 120° F., placed in a covered pan and set in a pressure chamber into which live steam is introduced at a pressure of say 100° giving a temperature around 330° F., and treated without agitation for say 12 hours. Afterwards it is run through rubber mixing rolls a number of times to bring it together and obtain the proper plasticity.

A representative formula using this material is:

	Per cent
Hard bitumen	43
Diatomaceous earth	38
Cotton linters	11
Softened tire peel	8

These materials may be mixed together as set forth hereinabove or otherwise as desired.

In the manufacture for example of a storage battery case it will be within the skill of the worker in the art both to vary the nature of his bituminous binder in order to compensate for an undesired softening effect of the rubber addition and also to effect economies in his binder as permitted by the toughening effect of the rubber additions thereto. As has been pointed out with any given binder the effect of the rubber, providing it is in homogeneous mixture and has not been too far broken down, is to give a somewhat softer composition as is measured by the ordinary hardness test, which composition will nevertheless be much more resistant to deflection under heat, much tougher, much less brittle and of substantially equal strength. So far as acid resistance is concerned, the addition of the rubber does not appear to have a great influence so that in the ordinary use of cotton fibers, for example, it is advisable to observe the quantitative limits laid down by Lukens in the binder referred to above. However, due to the additional toughness imparted by the rubber the quantity of vegetable fiber may be cut down arbitrarily without sacrificing toughness, or greater quantities of fiber may be employed if desired with longer mixing resulting in a greater acid proofing of the fibers with some mechanical disintegration thereof, since the added toughness imparted by the binder will compensate for this disintegration. Again mineral fibers such as asbestos material may frequently be employed in place of or in addition to the vegetable fibers because less toughening by long and strong fibers is needed. Thus tough boxes may be made with less vegetable fiber, and acid resistance obtained either by the use of acid resisting mineral fibers or by quantitative limitations of non-acid resisting mineral fibers, which has hitherto been impractical in battery boxes of this general type. Moreover, since with this type of binder toughness is not dependent upon hardness, there are wider variations possible in the quantities of filler materials which need be employed.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. A process of making molding compositions which comprises mixing a hard bituminous binder with filler and fibrous materials and during said mixing incorporating into the mass a quantity of rubber in softened condition at a stage in said process where the mechanical mixing still

to be done will be sufficient, having in regard the softened condition of said rubber, to incorporate said rubber into homogeneous admixture with said binder by the time of completion of said mix.

2. A process of making continuously thermoplastic molding compositions which comprises incorporating by intense mechanical action a relatively minor percentage of relatively unsoftened rubber material into a relatively major percentage of hard bitumen so as to form a homogeneous combined binder of thermoplastic characteristics, and afterwards incorporating filler and fibrous materials into said binder.

3. A process of making continuously thermoplastic molding compositions which comprises incorporating by intense mechanical action a relatively minor percentage of rubber material into a relatively major percentage of hard bitumen so as to form a fairly homogeneous mixture, and afterward incorporating filler materials into said mixture by a mixing operation proportioned so as to give at the end thereof a binder in which the bitumen and the rubber are in complete homogeneous admixture.

4. A process of making molding compositions which comprises making a mix of hard bitumen and filler materials, softening a rubber material, and mixing said softened rubber material into said mix so as to cause at least a major percentage thereof to come into substantially complete homogeneous admixture with said bitumen.

5. A process of making molding composition which comprises mixing a finely divided filler with a hard bitumen, adding thereto a rubber material and mixing it therewith to the extent of producing a combined, thermoplastic binder in which said rubber material and said bitumen are in substantially homogeneous admixture.

6. A process of making molding compositions which comprises making a mix of hard bituminous binder and filler materials and mixing therein a rubber substance of a consistency not more viscous than the bitumen under the conditions of mixing.

7. A process of making a continuously thermoplastic molding composition having a combined thermoplastic binder which comprises the steps of mixing a bituminous binder with a dispersion of rubber substances to an extent to drive off the dispersing agent therein and to bring said rubber substances substantially into homogeneous admixture with said bituminous binder, afterward adding filler materials to said combined binder.

8. A process of making a continuously thermoplastic molding composition having a combined thermoplastic binder which comprises the steps of mixing a bituminous binder with a solution of rubber substances to an extent to drive off the solvent therein and to bring said rubber substances substantially into homogeneous admixture with said bituminous binder, afterward adding filler materials to said combined binder.

9. A process of making molding compositions which comprises mixing filler materials with a thermo-plastic bituminous binder and after mixing therewith a quantity of rubber substance in the form of a dispersion, continuing the mixing to the extent of substantially homogeneously dispersing said rubber substances through said bitumen but limiting the extent of said mixing so as to avoid undue breaking down of the rubber substances.

10. A process of making molding compositions which comprises mixing filler materials with a thermo-plastic bituminous binder and after mixing therewith a quantity of rubber substance in the form of a solution, continuing the mixing to the extent of substantially homogeneously dispersing said rubber substances through said bitumen but limiting the extent of said mixing so as to avoid undue breaking down of the rubber substances.

11. A process of making molding compositions which comprises mixing rubber with a softening oil miscible with bitumen to the extent of softening said rubber, mixing a filler material with a hard bituminous binder and mixing into said mass a quantity of the said softened rubber to the extent of dispersing at least a substantial quantity of said rubber into homogeneous admixture with said bitumen.

12. A process of making molding compositions which comprises mixing rubber with a softening oil miscible with bitumen to the extent of softening said rubber, mixing a filler material with a hard bituminous binder and mixing into said mass a quantity of the said softened rubber to the extent of dispersing at least a substantial quantity of said rubber into homogeneous admixture with said bitumen, and afterward mixing a fibrous reinforcement into said mix.

13. A process of making a molding composition which comprises comminuting used rubber material, adding a softening oil thereto and treating said mixture with live steam until said rubber has been softened by said oil, afterward adding said softened rubber at least to the bituminous ingredient of a thermoplastic molding composition and mixing it therewith so as to form a combined thermoplastic binder in which the rubber is substantially in homogeneous dispersion throughout the body of the bitumen.

14. A process of making a molding composition which comprises comminuting used rubber materials and mixing these with a softening oil, treating the mixed mass with live steam under pressure until said rubber has been softened and running said mixed mass through a mill briefly so as to cause it to go together, afterwards mixing said mass at least with the bituminous ingredient of thermoplastic molding composition to the extent of bringing a substantial quantity of said rubber at least into homogeneous admixture in and dispersion throughout said bitumen.

15. A process of making a molding composition which comprises milling together rubber and relatively light bitumen substance so as to make a blend in which said rubber is softened and afterwards mixing said blend with at least the bituminous ingredient of a thermo-plastic composition to the extent of dispersing at least a major portion of said rubber homogeneously throughout the body of the said bitumen.

16. A process of making a molding composition which comprises milling together rubber and relatively light bitumen substance so as to make a blend in which said rubber is softened and afterwards mixing said blend with at least the bituminous ingredient of a thermo-plastic composition to the extent of dispersing at least a major portion of said rubber homogeneously throughout the body of the said bitumen, selecting as said bituminous binder a bituminous substance having sufficient hardness to offset the softening effect of said rubber blend to an extent sufficient to give the desired final hardness.

EDWARD R. DILLEHAY.