

UNITED STATES PATENT OFFICE

2,406,385

ABRASIVE ARTICLE AND METHOD OF
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ration of MassachusettsNo Drawing. Application April 1, 1944,
Serial No. 529,177

19 Claims. (Cl. 51-298)

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This invention relates to grinding wheels and other solid abrasive compositions and relates also to synthetic rubber compositions, and more particularly to the compounding and treatment thereof.

One of the objects of this invention is to provide a grinding wheel or other abrasive composition in which certain advantages of certain of the synthetic rubbers may be realized and in the manufacture and compounding of such abrasives certain disadvantages of such synthetic rubbers may be dependably overcome. Another object is to improve the workability of such synthetic rubbers, particularly for the incorporation therein of abrasive grains. Another object is to provide a practical and efficient method and compound for facilitating the breaking down of such synthetic rubbers and for overcoming certain inherent detrimental characteristics thereof, such as the crumbling and physical breaking up thereof when subjected to mill rolls.

Another object is to provide a dependable and practical method and compound for facilitating the handling, as on mill rolls, of rubber copolymers, such as various synthetics, as well as in subsequent processing operations for the making of abrasive articles, and more particularly to thereby overcome certain difficulties, shortcomings, and disadvantages inherent in certain heretofore proposed methods. Another object is to carry out this last-mentioned object in a manner to avoid the formation of water, such as is characteristic of certain prior attempts and as is detrimental to the structural and other characteristics of the grinding wheel or other abrasive article. According to certain prior attempts to improve the workability of synthetic rubbers and the making of abrasive articles, particularly in the butadiene co-polymers, substantially uncontrollable reactions immediately set in resulting in such disadvantages as the inherent imposition of time limitations upon various steps in the processing, a hardening or drying up of the mix, substantially prematurely, resulting in mechanical crumbling or loss of plasticity or hardening as to make the batch or mix useless or inherently wasteful and inefficient. Another object is to overcome such deficiencies and disadvantages, in such prior attempts, as cause material loss because of impossibility or exorbitant costliness of

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recovery of so-called scrap or like surplusage resulting from molding or cutting out or otherwise forming the mix into the desired shape of abrasive article.

Another object is to provide abrasive articles of the above-mentioned nature that can be given characteristics that combine certain features of the characteristics of rubber-bonded wheels and certain features of the characteristics of resin-bonded wheels. Another object is to provide an abrasive bond that is compounded out of both synthetic rubbers and resins and in which certain advantages of both of these ingredients can be successfully realized. Another object is to provide a method of compounding and curing abrasive articles so compounded that will be simple and expedient to carry out in large scale manufacture and that will be dependable and reliable. Another object is to provide a method of compounding and curing abrasive articles compounded out of ingredients that include synthetic rubbers and heat-responsive resins, in such a way that the synthetic rubbers may be dependably plasticized or worked up into suitably plastic condition and admixed with resins without giving rise to the formation of water, without having hardening or setting reactions take place prematurely or at temperatures at which, for efficient manufacture, certain steps in the processing are carried out, or without having to cope with such other detriments of prior attempts as drying out, crumbling, or mechanical break-up, and the like.

Other objects will be in part obvious or in part pointed out hereinafter.

The invention accordingly consists in the features of construction, combinations of elements, arrangements of parts, and in the several steps and relation and order of each of said steps to one or more of the others thereof, all as will be illustratively described herein, and the scope of the application of which will be indicated in the following claims.

It has been found that the synthetic rubbers, known collectively as butadiene polymers, including co-polymers, and known commercially collectively by the trademark "Buna," do not respond to all aspects of natural rubber technique in working them up for the making of abrasives, that some of them do not effectively break down

or plasticize when worked on mill rolls, that others, though exhibiting tendencies toward plasticizing, cannot efficiently or commercially be plasticized by simple milling, and that in these and other respects they present problems, obstacles or difficulties of one kind or another when they are attempted to be used in the making up of abrasive articles.

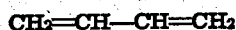
These Buna type of rubbers, when put on mill rolls, instead of plasticizing or becoming plastic, doughy or flowable, become in varying degrees crumbly and in fact break up into lumps and in that sense physically disintegrate, making it difficult or impossible to continue the milling operation, since the material refuses to hug the mill rolls and the pieces or particles that crumble off of it cannot effectively be handled for restoration to the mill rolls. As a result also abrasive grain cannot be at all or efficiently worked into the material on the mill rolls.

Furthermore, certain plasticizing agents heretofore attempted to be used, such as furfural, and other unsaturated aldehydes and unsaturated alcohols, have numerous disadvantages, such as, for example, the frequent production of too much stickiness or tackiness, resulting in difficulty in working the synthetic rubber up on mill rolls, also the setting in of reaction with the added resin or resins at such a high rate and even at ordinary room or working temperatures that the mix undergoes curing or dries out and becomes hard and crumbly, precluding further workability, and also the formation during the reaction, of water which can and usually does cause swelling or bloating in the grinding wheel structure and otherwise detrimentally affects the structure and function of the abrasive article.

The above appear to be characteristic deficiencies or obstacles of the butadiene polymer and co-polymers and of prior attempts to plasticize them and incorporate resins with them, and a dominant aim of this invention is to overcome these difficulties and to make possible the efficient and practical incorporation of these synthetics into abrasive articles.

As above pointed out, I contemplate the use in my invention not only of polymeric butadiene but also co-polymers of butadiene, and amongst other ingredients that I employ in admixture therewith, I use a suitable vulcanizing agent which is preferably sulphur. The more familiar butadiene co-polymers are the co-polymers of butadiene with acrylic nitrile, usually vulcanized with sulphur and the co-polymer of butadiene with styrene, usually vulcanized with sulphur, though it will be understood that methyl acrylic nitrile may be employed in place, for example, of acrylic nitrile.

Butadiene is a hydrocarbon of the formula,



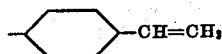
Butadiene is considered to polymerize in a linear chain. Acrylic nitrile may be also termed vinyl cyanide and is written,



Methyl acrylic nitrile may be written,



and has properties similar to acrylic nitrile. It may be termed methyl vinyl cyanide. Styrene is written,



and may be termed vinyl benzene. Thus all three of acrylic nitrile, methyl acrylic nitrile and styrene have a vinyl or a substituted vinyl group. These substances link together with butadiene in the chains and together form a linear polymer. When sulphur is added, however, and the compound is vulcanized, there is a cross linking more or less, depending upon the amount of sulphur used. The butadiene polymers, whether butadiene alone or copolymerized with acrylic nitrile, methyl acrylic nitrile or styrene, are thermoplastic until vulcanized with sulphur. The subsequent reaction or polymerization or copolymerization thereof with a vulcanizing agent, usually sulphur, is achieved by the use of heat and may be termed vulcanizing.

Of the above butadiene polymers, the co-polymer of butadiene with acrylic nitrile is available on the market under trade names "Perbunan," "Chemigum 1," and "Hicar OR 15"; the butadiene co-polymer with styrene is represented commercially by synthetic rubbers known under the trade-marks or designations "Buna S," "Hicar OS 10," "Hicar OS 20" and "Hicar OS 30." These evidence such undesirable characteristics as those noted above when subjected to the mill rolls in the endeavor to plasticize them. These various co-polymers have somewhat differing characteristics due principally to substantially correspondingly different proportions of acrylic nitrile or styrene initially employed in achieving the co-polymer and probably for these and possibly other reasons they evidence the just-mentioned undesirable characteristics to varying extents.

In the practicing of my invention I am enabled to achieve adequate practical or efficient plasticizing of the butadiene polymers by plasticizing agents which not only overcome the above-mentioned undesirable characteristics of the butadiene polymers but also are brought into coaction with other ingredients that I prefer to employ, preferably coaction by cross-linking with such additional ingredients. Additional ingredients for this purpose are preferably thermo-responsive resins and preferably I achieve a suitably delayed cross-linking in order to avoid tendency to harden during milling, calendering, shaping, molding or the like and also to achieve other advantages, all as is more clearly set forth herein-after.

The practicing of my invention, in its various aspects and also to give certain specific illustrations of certain of its advantages, will be understood by considering the making of an abrasive composition, such as a grinding wheel. Accordingly, I start with a suitable quantity of abrasive grain of any suitable kind. Thus I may employ any of the varieties of alumina, such as emery, corundum, dense "regular" fused alumina, porous white fused alumina; silicon carbide and other hard carbides; quartz; glass; garnet; or diamonds. These are illustrations and, of course, two or more of these abrasives may be mixed, if desired. Such abrasive grain is to be bonded to form, for example, a grinding wheel.

A suitable quantity of the butadiene polymer is now put onto the mill rolls to be worked and milled and a liquid plasticizing agent is immediately added thereto and added from time to time as the milling proceeds, appropriately proportioned in amount in relation both to the plasticizing needs of the butadiene polymer and to the resin with which it is subsequently to coact. This agent softens the butadiene polymer which with the aid of the agent and under action of the mill

rolls becomes suitably plastic or doughy and of a consistency and texture so that it will hug the rolls. For purposes of illustration at this point, the plasticizing agent can comprise tri-glycol dichloride and its action upon the synthetic or butadiene polymer is as just stated.

Having worked the material appropriately on the mill rolls, the resin is added thereto in powdered form and the resin that is added and the already added plasticizing agent, such as tri-glycol dichloride, are subsequently to react with each other, the plasticizing agent acting as a cross-linking and hardening agent for the resin, all as is later described.

On the mixing or milling rolls, the powdered resin becomes thoroughly distributed throughout the mass and next the vulcanizing agent is added and in the case of the butadiene polymers or Buna types of synthetic rubber the preferred vulcanizing agent is sulphur. That is added in powdered form and also becomes distributed throughout the still plastic mass and next the desired quantity of abrasive grain is added, the above-described steps, explained in greater detail later, having also conditioned the plastic mass for the admixture therewith of the abrasive grains.

As conducive to a clearer understanding of certain features of my invention, it might at this point be noted that a usual grain-wetting and resin plasticizing or hardening agent to employ in the making up of a phenolic resin-bonded abrasive is furfural, but furfural I have found does not plasticize all of the Buna rubber compounds above mentioned and even if it did, its presence in the ultimate mix along with phenolic resin would result in the commencement and progression of setting or curing of the resin, resulting in a hardening that would necessitate very rapid procedure and immediate shaping and heat treatment of the green abrasive mix. On the other hand, tri-glycol dichloride and other plasticizers for the Buna that I employ do not cross-link with the phenolic resins and hence, in employing phenolic resins in my invention, such resins are first treated so that these plasticizers, having functioned on the mill rolls to soften and plasticize the Buna rubber compound, will ultimately cross-link therewith and preferably with the application of sufficient heat, thus avoiding also cold-setting.

Such treatment of the phenolic resins is effected that will make available in them for cross-linking during polymerization under subsequent heat treatment nitrogen atoms in the resin polymer molecule to which the plasticizing and hardening agent, illustratively the above-mentioned tri-glycol dichloride, can link or attach itself to form an adequately cross-linked polymer which is a hardened tough resin body. The same heat treatment that effects such cross-linking effects also vulcanization of the butadiene polymer or polymers that are employed.

With such a hardening agent and with a phenolic resin compounded with, or supplemented by, ingredients or compositions so that an amino group or a nitrogen atom is not available for such attachment or cross-linking to or with the hardening agent until a sufficiently high temperature above room or working temperatures is achieved (as in subsequent heat treatment for vulcanization of the polymerized butadiene), the progressive hardening at room or working temperatures inherent in known methods of molding phenolic resin products therefore does not or cannot take

place or takes place at room or working temperatures only at such a low rate as will still permit achievement of the advantages and benefits of my invention.

There is a goodly number of ways in which a phenolic resin can be aminated, thus to make available an amino group or nitrogen atom for subsequent cross-linking with a hardening agent of the above-mentioned kind. For example, phenol and formaldehyde and ammonia (NH_3) may be reacted, and the resultant potentially reactive resin would be suitable to add to the mix on the mill rolls and to function according to my invention; the ultimate or end product can be made to be fusible or permanently infusible according, as is known, to the proportion of phenol and formaldehyde initially employed. In such a condensation reaction, the ammonia acts primarily as a catalyst but it also acts as an aminating agent, bringing into the resin molecule polymer an amino or nitrogen atom group.

Another way of providing the nitrogen atoms for ultimate cross-linking or co-polymerization with a hardening agent of the above-mentioned character to form a hard resinous body is to employ, in powdered form, an admixture of potentially reactive phenolic resin, such as phenol formaldehyde, and hexamethylenetetramine, hereinafter referred to simply as "hexa"; such an admixture is sometimes regarded as a solid solution of the hexa in the resin and is, moreover, available on the market under the designation "Bakelite BR 2417," a product of Bakelite Corporation. In producing such potentially reactive resin, the hexa is mixed with the phenol formaldehyde, the mixture is melted and, after cooling, the resultant solidified mass is broken up and powdered for use. In such powdered form, the hexa is in solution in the resin and is available for aminating the resin during subsequent heat treatment during which, also, the hardening agent employed first to plasticize the butadiene polymer on the mill rolls according to my process subsequently cross-links under heat treatment with the aminated resin at the nitrogen groups thereof.

Or, depending, for example, upon the characteristics desired in the end product, phenol and formaldehyde and ammonia may be reacted in the manner above described and to the resultant potentially reactive resin, preferably in powdered form, a suitable quantity of hexa is added, also in powdered form; the former is aminated during the condensation or reaction in the presence of ammonia and the latter can function as an aminating agent during the subsequent heat treatment of the resultant mix in admixture with the plasticizing and hardening agent, the heat treatment effecting also vulcanization of the synthetic rubber.

Amination of the phenolic resin may also be effected by adding a suitable quantity of aniline to the phenol and then reacting with formaldehyde in the presence of a catalyst which may be sodium hydroxide, calcium hydroxide, or, by way of further example, ammonia.

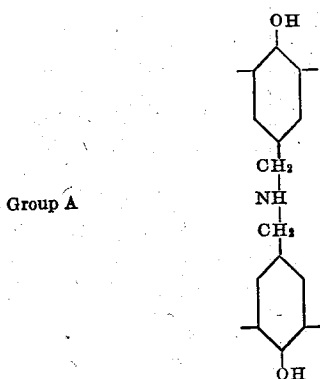
Or phenol and formaldehyde may be reacted in the presence of an aliphatic amine (in place of the ammonia in the first above-described illustration), and any suitable aliphatic amine may be employed, such as methyl amine, ethyl amine, propyl amine, etc.

Amination of the resin may thus be effected prior to or during final heat treatment or in point of time, the one may supplement the other,

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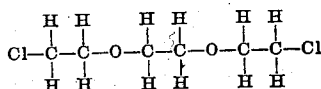
as in the case of the third above-described example; unless otherwise qualified, therefore, the terms "aminated" or "aminating" or "aminated" as used in the claims are intended to be generic and without regard to the specific time, stage, or step in which amination of the resin polymer molecule takes place.

It is therefore a phenolic resin that is aminated or capable of amination under subsequent heat treatment that I add on the mill rolls after the liquid plasticizing agent has served in coaction with the mill rolls to soften and plasticize the polymerized butadiene and, as above noted, the vulcanizing agent, such as sulphur, and the abrasive grains are also added and a thorough intermixing thereof is achieved. Subsequent sheeting out, as on calender rolls, to the desired thickness is then effected and from the sheet the desired shape of abrasive material, such as a disk for a grinding wheel, is cut out and the resultant cut-out green abrasive shapes are then heat treated not only to effect vulcanization of the polymerized butadiene but also to achieve cross-polymerization between the resin and the plasticizing-hardening agent. Considering more in detail the reactions that take place, let it again be considered that the above-described phenolic formaldehyde resin with hexa is added to the mix after tri-glycol dichloride had been added to plasticize the uncured butadiene polymer. The presence of the nitrogen atom in the potentially reactive phenol formaldehyde resin is due to the fact that the reaction of the resin (phenol formaldehyde in the above-assumed illustration) and the hexa produced some groups of the following type, hereinafter called, for convenience, Group A:



In the above, note the NH or nitrogen atom group, available for cross-linking.

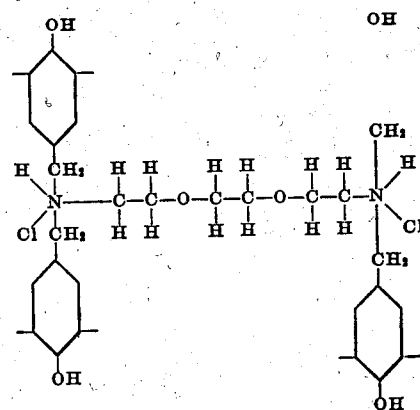
Tri-glycol dichloride is written thus:



At ordinary or room temperatures or the temperatures that exist during making up of the mix or in working it on mill rolls, calender rolls or the like, the tri-glycol dichloride and the phenol formaldehyde resin polymer which is alkylated by the hexa so that a nitrogen atom is introduced into the resin polymer molecule as above explained and as appears from the above Group A or chain above depicted, there is no reaction between the two, that is, no substantial or material cross-linking between the two takes place, and hence the desired state of plasticity or condition of flowability of the entire mix is re-

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tained. But when subjected to heat treatment to effect vulcanization of the polymerized butadiene, and illustrations of which are set forth hereinafter, the reaction between the two sets in and a highly cross-linked structure and hard, tough resinous product result. Such cross-linking forms groups of the following type:

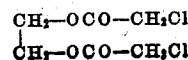


It will be noted that the plasticizing or hardening agent cross-links with A groups at the amino groups of the latter, specifically at the NH or N atom groups, and without the provision of the latter, the tri-glycol dichloride would not function as it does as a resin-hardening agent. It will thus be noted that the phenol formaldehyde resin, in being thus provided with a nitrogen atom or atoms in its continuous chain groups, is thus prepared or conditioned structurally, in a chemical sense, for reaction and cross-linking with the tri-glycol dichloride and that such preparation can be effected as well as final cross-linking with the tri-glycol dichloride, not only without detracting from the ultimate desirable qualities of the hardened resin, but also with the achievement of new characteristics, such as absence of detrimental stickiness, maintenance of plasticity or flowability of the whole mix before final heat treatment, and the like.

Moreover, it will also be noted that the tri-glycol dichloride has functioned as a halogenating agent, H and Cl appearing in the groups of the cross-linked polymer at the amino groups thereof. This is advantageous when making abrasive products, such as grinding wheels, for the heat generated at the grinding line causes the release from the structure of hydrogen chloride, thus coacting to achieve improved or better grinding action.

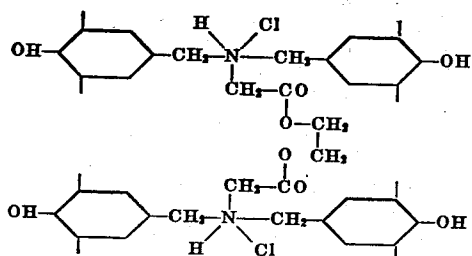
Numerous other substances may be employed, besides tri-glycol dichloride. Thus I may use dichlor diethyl ether; other poly-glycol dichlorides may also be used, for example, tetra-glycol dichloride, or penta-poly-glycol dichloride, and of course, mixtures of two or more may also be employed. Compounds of large molecular weight, that is, having additional C_2H_4 groups, are solids and, without more, cannot take part in making up a plastic or flowable mass and hence it is preferred not to use them.

Other cross-linking agents that may be employed, and there are many, include di-monochloracetates of ethylene glycol, poly-ethylene glycol, substituted poly-ethylene glycols and trimethylene glycol; di-monochloracetate of ethylene glycol is:



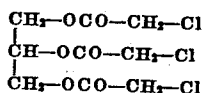
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Cross-linking with the nitrogen-atom containing phenolic resin, containing the above-mentioned groups A, again takes place at the nitrogen atoms of the resin polymer molecule and again halogenation takes place in that H and Cl appear in the groups of the cross-linked polymer at the amino groups thereof, in substantially the following way which illustrates, with respect to di-monochloracetate of ethylene glycol how the other above-mentioned agents also cross-link.

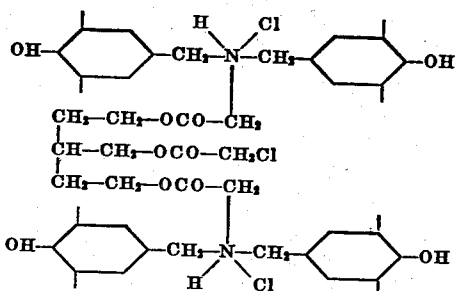


The just-mentioned substances might all be called glycol di-monochloracetates and of the latter, it is preferred to use any glycol di-monochloracetate selected from the group consisting of ethylene glycol di-monochloracetate, di-ethylene glycol di-monochloracetate, tri-ethylene glycol di-monochloracetate, and tri-methylene glycol di-monochloracetate.

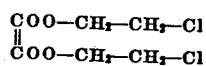
Still other substances usable in the above manner may comprise tri-monochloracetates of certain trihydric alcohols, more particularly in the use of glycerol tri-monochloracetate or tri-methylol propane tri-monochloracetate, or mixtures thereof. Glycerol tri-monochloracetate is written thus:



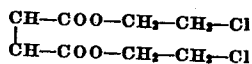
The latter may be used to illustrate the cross-linking of ingredients of the above-mentioned group, substantially as follows:



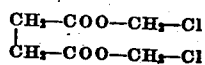
Also, esters of ethylene chlorhydrins with polybasic acid may be used; thus, I may use, di-2-chlorethyl phthalate; this ester is:



Or I may use di-2-chlorethyl maleate; this ester is:

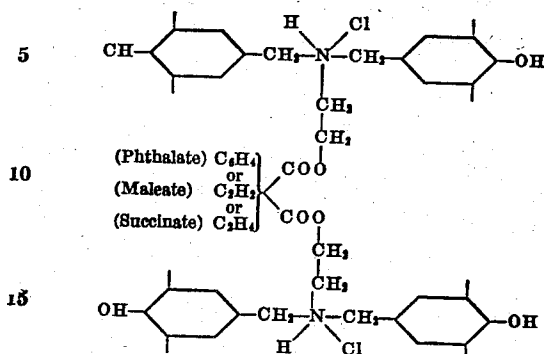


Or I may use di-2-chloroethyl succinate; this ester is:

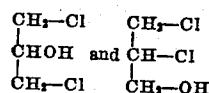


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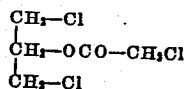
The cross-linking may be set out substantially as follows:



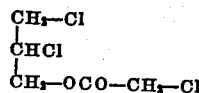
20 Other usable esters comprise chloracetates of glycerol chlor-hydrins or mixtures thereof and conveniently a mixture is employed; for example, I may start with glycerol $\alpha\gamma$ dichlorhydrin and glycerol $\alpha\beta$ dichlorhydrin, which are, respectively, or may be written thus:



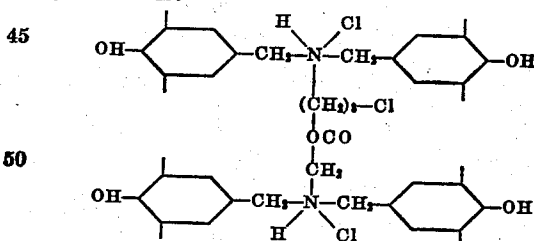
30 Mixtures of the above form chloracetates when reacted with chloracetic acid; such chloracetates are, respectively, or may be written thus:



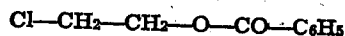
and



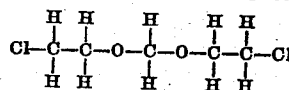
Cross-linking of the mixture with the nitrogen-bearing phenol formaldehyde resin is substantially like this:



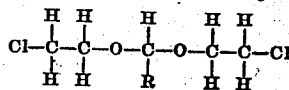
2-chlorethyl benzoate may also be used; it may
55 be written as:



Still other substances usable in the above manner may comprise acetals, such as di-2-chlorethyl formal, di-2-chlorethyl benzal, di-2-chlorethyl enanthal, di-2-chlorethyl propanal, di-2-chlorethyl furfural and di-2-chlorethyl butyral. Of these substances, di-2-chlorethyl formal may be set out as an example; this acetal is:



These acetals have generally similar characteristics and may be represented by the formula:

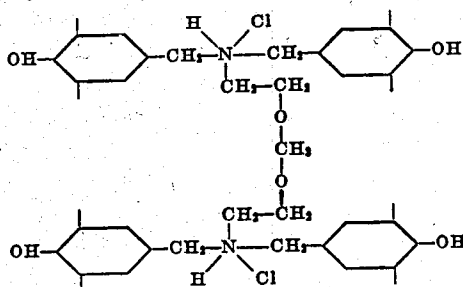


75 where R is hydrogen or aryl, alkyl, aralkyl group

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containing 7 carbon atoms or less, or is a heterocyclic carbon radical containing 4 carbon atoms.

The cross-linking that results when such an acetal is employed, with the nitrogen-bearing phenol formaldehyde resin may be illustrated, with the formal, like this:



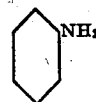
Thus it will be seen that there are numerous compositions that can be employed; these agents are all liquid plasticizers for the polymerized butadiene and are also hardening agents for the resin; they are cross-linking agents and, moreover, will be seen to have the characteristic that their attachment is at the nitrogen atom or nitrogen group with which the resin polymer molecule has been provided by alkylation of the phenol formaldehyde resin; they are all halides and thus are well suited to cross-linking at or attachment to the nitrogen atom group in the resin polymer molecule. They also halogenate the resin which is the end product and this is of advantage in the making of abrasive articles in that the grinding action, due to the release, in the above illustrations, of hydrogen chloride, is improved. In no case is H_2O formed. In each case, the H and Cl appears attached at the nitrogen atom group. Naturally enough, the examples above set forth are chlorinated compounds because these are cheaper and more readily available or produceable than other halogenated compounds, such as the brominated or iodated, but halogenated compounds other than the chlorinated will give effective results and the setting forth of such chlorinated compounds as the above is not to be interpreted by way of limitation.

The use in the above illustrations of phenol formaldehyde resin is not by limitation but is simply illustrative of a resin with which the above-mentioned agents, which function well as plasticizers for the synthetic rubber, do not react unless the resin is first aminated to provide it with a nitrogen group at which these agents can react for polymerization to effect hardening of the resin concurrently, or substantially so, with the vulcanization, under heat treatment, of the rubber in the molded or shaped mix. Other resins that can be made potentially reactive, as by aminating them as above described in connection with phenol formaldehyde resin, are other phenol aldehyde resins, such as phenol furfural, cresol formaldehyde and cresol furfural. But there are other resins with which these plasticizing and hardening agents are reactable directly, that is, without such pre-treatment as amination, and such resins are amine aldehyde resins of which illustrative embodiments as well as illustrative examples of reaction with illustrative plasticizing agents taken from those above mentioned may now be considered.

Thus, I provide a quantity of a primary aromatic amine, such as aniline, ortho, meta or para toluidine, or diamino diphenyl methane; and a quantity of formaldehyde. I may option-

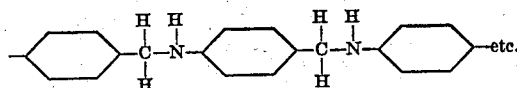
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ally provide a quantity of one or more organic compounds containing halogen selected from the group consisting of chlorine, bromine and iodine and capable of splitting off hydrogen halide at elevated temperatures and/or of alkylating an aromatic amine polymer, providing cross links connecting amine groups of the chains. The aromatic amine which I now prefer to use is aniline. Aniline



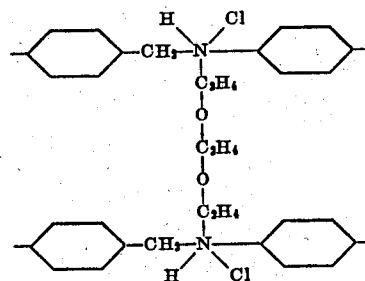
or one of the other aromatic amines mentioned, or mixtures of two or more of such amines, is reacted with formaldehyde $HCHO$ in the presence of a strong acid to produce a long chain polymer which, when an excess of formaldehyde above the stoichiometric proportions is used, for example, 20% excess, has adjacent chains connected with methylene $-CH_2-$ groups to form a tough, heat resistant, semi-thermoplastic resin. I may add some of the formaldehyde after the initial condensation, in the form of paraformaldehyde, or by the addition of hexamethylene-tetramine.

A stoichiometric quantity of aniline and formaldehyde condensed in the presence of a strong acid is believed to produce a resin which is structurally represented thus:



It is such a resin which in powdered form may be added to the mix or material that has been worked up on the mill rolls and that comprises the synthetic rubber and any of the plasticizing agents therefor, above described; on the mixing or mill rolls, the powdered resin becomes thoroughly distributed throughout the mass of doughy or plastic butadiene polymer or co-polymer, a suitable vulcanizing agent, preferably sulphur, is next added and that also becomes distributed throughout the still plastic mass, whence the desired quantity of abrasive grain is added. The mass is suitably shaped and then given heat treatment to effect vulcanization of the synthetic rubber and to bring about reaction between the synthetic-rubber-plasticizing agent and the resin, cross-linking taking place between the resin polymer and the hardening agent. Illustrative cross-linkages are set out below:

Thus, where the plasticizer for the butadiene polymer or co-polymer is tri-glycol dichloride, the cross-linking with the resin polymer that takes place while vulcanization goes on may be represented as follows, where the resin is the above-mentioned illustrative aniline formaldehyde polymer:

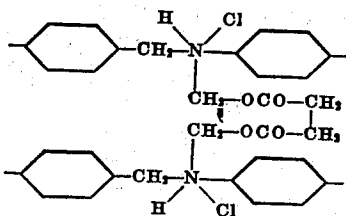


It will be noted that the chlorine now appears at the amino groups of the resultant cross-linked

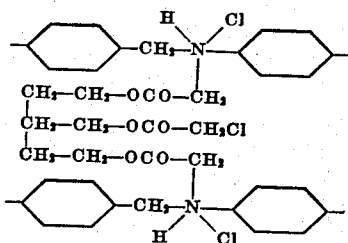
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polymer; heat generated at the grinding line during operation of the grinding wheel causes the release from the structure of hydrogen chloride, thus coacting to achieve improved or better grinding action, preventing or lessening "loading" and assisting in the cutting action by making the metal chips more brittle. Again no H_2O is formed and no swelling on that account takes place. Cross-linking does not take place during room temperatures or during temperatures created in making up the mix as on mixing or mill rolls or if it takes place at all happens at such a low rate as to be substantially immaterial and still permit the achievement of the advantages and benefits of my invention. Likewise, the mixture does not get dry or hard or crumbly and as is the case with the phenolic and similar resin types earlier above mentioned, scraps of the mix or surpluses resulting from molding or cutting out from sheet form can be collected and stored, without hardening, to be re-used. Unduly short time limitations are thus not imposed upon the processing to completion of abrasive articles and thus many production advantages and savings are achieved.

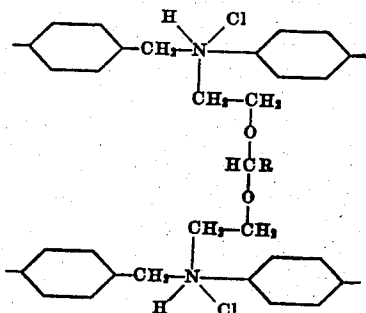
Again using aniline formaldehyde polymer as an illustrative resin and to illustrate its cross-linkage with another synthetic-rubber-plasticizing agent, such as the di-monochloracetate of ethylene glycol, the cross-linking may be set out as follows:



A similar illustration in the case of glycerol tri-monochloracetate gives a cross-linkage as follows:



The cross-linkage with the aniline-formaldehyde polymer, during the vulcanization heat treatment of the formed or shaped mix, with the above-mentioned acetals may be represented as follows:



The above illustrations of cross-linkages where the resin is an amine formaldehyde resin will suffice to show the manner of cross-linking where others of the synthetic-rubber-plasticizing agents

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than those specifically set out in the cross-linkages are employed.

From the above the practice of my invention will now be clear. The butadiene polymer, either the polymer or co-polymer, may be worked up on mixing or mill rolls in a thoroughly efficient and practical way conducive to dependable quantity production in that, for example, the plasticizing agents my invention provides achieve a plasticity of the synthetic rubber that is devoid of troublesome or detrimental stickiness, such as occurs when compositions like the earlier above-mentioned furfural are attempted to be employed to plasticize the Buna type of polymer, and these desirable qualities are maintained during subsequent mixing or milling as when the powdered resin and vulcanizing agent, such as sulphur in powdered form are admixed therewith. These desirable characteristics or features of the resultant plasticity or flowability under pressure of the whole mix are moreover maintained in spite of rise in temperature during milling and in spite of the passage of the time element; thereby also I achieve and maintain those desirable characteristics in the mix whereby the abrasive grain, when added thereto, is with facility and adequate speed taken up by the doughy plastic mass and the individual grains properly and completely enveloped and "wetted" by the plastic mix, thus conditioning the uniquely coacting ingredients to achieve, during the subsequent curing heat treatment, strong, efficient and complete bonded envelopment and gripping of the many individual abrasive grains. These same desirable characteristics make possible also the admixture into the mix undergoing mixing or milling of any of a wide variety of filler material well known in the art so that specific examples need not here be given, but the particles of the filler become enveloped within and by the plastic mix in a manner much the same as are the abrasive grains. Thus a high quality of bond is achievable, not only of the desired strength, but also of uniformity of strength throughout the ultimate structure of the abrasive wheel or other article.

Where materials like furfural are employed, reaction with the resin at once sets in, accelerated by the heat produced during mixing or milling and the resultant drying and hardening progressively removes or diminishes whatever receptivity the mass might have had for the reception of abrasive grains, fillers or the like, and the progressing reaction thus imposes cumulative or multiplying disadvantages in that, for example, the speed of the reaction of drying and hardening imposes speedier milling only to result in more rapid heat production with consequent acceleration of the hardening reaction, etc., etc. Such disadvantages are furthermore, complicated or increased where certain particular grinding wheel compositions are sought to be produced, such as for example, high volume percentage of abrasive grain, or high volume percentage of filler; in such cases, the milling and mixing operation, to achieve uniformity of distribution, necessarily takes a longer time and during that longer time, accompanied by continued heat production, a more rapid or a greater drying out and hardening reaction takes place. Crumbling and mechanical or physical breaking up of the mix can follow, with complete failure of result. Even where successful, the reaction of compounds like furfural with the resin produces water, resulting in bloating and swelling during curing heat treatment and otherwise resulting in a mechanically

weak structure and also in functional impairments.

Illustrative proportions that can be employed comprise, by way of example, 100 grams of OS 10, 50 grams of sulphur, 125 grams of BR 2417 resin and 42 grams of tri-glycol dichloride. Fillers may be added as desired. The resultant mix is shaped in any desired way and is then given suitable heat treatment conjointly to react the resin with the plasticizing hardening agent and to effect vulcanization by reaction of the butadiene polymer with the vulcanizing agent which in the above illustration is the sulphur.

In the above illustration, instead of the tri-glycol dichloride any of the above mentioned plasticizing and hardening agents or their equivalents may be employed; instead of the OS 10, any of the butadiene polymers (which include the polymer and the co-polymers) or their equivalents may be used; instead of sulphur, any suitable vulcanizing agent for such polymers may be substituted; and instead of the specified BR 2417 resin any other of the numerous resins above mentioned or their equivalents may be employed. The proportions can vary widely according to the particular combination of ingredients employed and according to the abrasive structure desired, and other ingredients, such as fillers, boosters, accelerators, activating agents, stabilizers or the like may be added or employed. The resultant grinding wheel structures are of good performance, are of good quality numbers, and can be compounded to have low wheel wear per unit of metal or other material removed during grinding operation. A wide variety of grinding wheel structures to meet widely varying practical grinding requirements and conditions is achievable and in the processing of such structures numerous thoroughly practical manufacturing advantages, some of which are pointed out above, are achieved.

By my invention production is greatly facilitated, difficulties and disadvantages of prior attempts are overcome, and substantial savings can be effected. For example, cold-setting or reaction of the resin constituent with the plasticizing and hardening constituent, at room temperatures or at normal working temperatures prior to final heat treatment, does not set in or if it takes place at all happens at such a low rate as to be substantially immaterial or as will not interfere with normal and intended production or manufacturing steps. Un-molded or un-shaped mixes may thus be carried over as from one day to the next or to await a subsequent series of molding or sheeting out and cutting out operations, also left-over portions of mixes and particularly scraps where the mix is sheeted out and then cut out in disk or other form can be collected and stored or otherwise held for re-use, and thus material wastage of already processed material can be avoided.

It will thus be seen that there has been provided by this invention an abrasive product and method of making the same in which the various objects hereinabove set forth together with many thoroughly practical advantages are successfully achieved. As many possible embodiments may be made of the mechanical features of the above invention and as the art herein described might be varied in its various parts, steps, relation and order of each of the same to one or more of the others thereof, all without departing from the scope of the invention, it is to be understood that all matter hereinabove set forth is to be inter-

preted as illustrative, and not in a limiting sense.

I claim:

1. The steps in the method of making an abrasive article which comprise improving the workability of an unvulcanized butadiene polymer by treating it during working with a halogen-bearing plasticizing agent in which the halide is selected from the group consisting of chlorine, bromine and iodine and which is substantially non-reactive with the polymer but capable of softening and making the polymer plastic under mechanical working thereof for the reception therein of abrasive grain; distributing into and throughout the plasticized butadiene polymer a vulcanizing agent, abrasive grain, and a resin polymer having amino groups therein and with which resin polymer the halogen-bearing plasticizing agent is capable of reaction at elevated temperatures and at the amino groups thereof to harden it but is incapable of substantial reaction at working temperatures of the resultant mix; shaping the mix; and under heat treatment of the shaped mix, reacting the halogen-bearing agent at the amino groups of the resin polymer to harden the resin and vulcanizing the butadiene polymer by reacting with the vulcanizing agent.

2. The steps in the method of making an abrasive article which comprise improving the workability of an unvulcanized butadiene polymer by treating it during working with a halogen-bearing plasticizing agent in which the halide is selected from the group consisting of chlorine, bromine and iodine and which is substantially non-reactive with the polymer but capable of softening and making the polymer plastic under mechanical working thereof for the reception therein of abrasive grain; distributing into and throughout the plasticized butadiene polymer a vulcanizing agent, abrasive grain, and an aminated potentially reactive phenolic resin with the polymer of which the halogen-bearing plasticizing agent is capable of reaction at elevated temperatures and at the amino groups thereof to harden it but is incapable of substantial reaction at working temperatures of the resultant mix; shaping the mix; and under heat treatment of the shaped mix, reacting the halogen-bearing agent at the amino groups of the aminated resin polymer to harden the resin and vulcanizing the butadiene polymer by reacting with the vulcanizing agent.

3. The steps in the method of making an abrasive article which comprise improving the workability of an unvulcanized butadiene polymer by treating it during working with a halogen-bearing plasticizing agent in which the halide is selected from the group consisting of chlorine, bromine and iodine and which is substantially non-reactive with the polymer but capable of softening and making the polymer plastic under mechanical working thereof for the reception therein of abrasive grain; distributing into and throughout the plasticized butadiene polymer a vulcanizing agent, abrasive grain, and an amine formaldehyde resin polymer with which the halogen-bearing plasticizing agent is capable of reaction at elevated temperatures and at the amino groups thereof to harden it but is incapable of substantial reaction at working temperatures of the resultant mix; shaping the mix; and under heat treatment of the shaped mix, reacting the halogen-bearing agent at the amino groups of the resin polymer to harden the resin and vulcaniz-

ing the butadiene polymer by reacting with the vulcanizing agent.

4. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising butadiene polymer, a vulcanizing agent therefor, a resin polymer having amino groups, and a halogen-bearing butadiene-polymer-plasticizing and resin-polymer-hardening agent in which the halide is selected from the group consisting of chlorine, bromine and iodine, the butadiene polymer being vulcanized by reaction with the vulcanizing agent and the resin polymer being hardened by reaction at the amino groups thereof with the halogen-bearing plasticizing agent.

5. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising butadiene polymer, a vulcanizing agent therefor, an aminated phenolic resin, and a halogen-bearing butadiene-polymer-plasticizing and resin-polymer-hardening agent in which the halide is selected from the group consisting of chlorine, bromine and iodine, the butadiene polymer being vulcanized in reaction with the vulcanizing agent and the resin being hardened by reaction at the amino groups thereof with the halogen-bearing plasticizing agent.

6. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising butadiene polymer, a vulcanizing agent therefor, a primary aromatic amine formaldehyde resin polymer, and a halogen-bearing butadiene-polymer-plasticizing and resin-polymer-hardening agent in which the halide is selected from the group consisting of chlorine, bromine and iodine, the butadiene polymer being vulcanized by reaction with the vulcanizing agent and the resin being hardened by reaction at the amino groups thereof with the halogen-bearing plasticizing agent.

7. The steps in the method of making an abrasive article which comprise mixing abrasive grain, butadiene polymer, a vulcanizing agent, a resin polymer having amino groups therein, and a halogen-bearing resin-hardening agent in which the halide is selected from the group consisting of chlorine, bromine and iodine and which is reactable under heat treatment with the resin polymer at the amino groups thereof and capable of softening the butadiene polymer; working the mix to effect softening of the butadiene polymer by the halogen-bearing resin-hardening agent to improve the plasticity of the butadiene polymer for mechanical assimilation throughout of the abrasive grain; shaping the mix to give it the desired configuration of abrasive article; and by heat treatment of the shaped mix, vulcanizing the butadiene polymer and reacting the resin polymer at the amino groups thereof with said halogen-bearing agent.

8. The steps in the method of making an abrasive article which comprise mixing abrasive grain, butadiene polymer, a vulcanizing agent, an aminated phenolic resin, and a halogen-bearing resin hardening agent in which the halide is selected from the group consisting of chlorine, bromine and iodine and which is reactable under heat treatment with the resin polymer at the amino groups thereof and capable of softening the butadiene polymer; working the mix to effect softening of the butadiene polymer by the halogen-bearing resin-hardening agent to im-

prove the plasticity of the butadiene polymer for mechanical assimilation therethrough of the abrasive grain; shaping the mix to give it the desired configuration of abrasive article; and by heat treatment of the shaped mix, vulcanizing the butadiene polymer and reacting the resin polymer at the amino groups thereof with said halogen-bearing agent.

9. The steps in the method of making an abrasive article which comprise mixing abrasive grain, butadiene polymer, a vulcanizing agent, a primary aromatic formaldehyde resin, and a halogen-bearing resin-hardening agent in which the halide is selected from the group consisting of chlorine, bromine and iodine and which is reactable under heat treatment with the resin polymer at the amino groups thereof and capable of softening the butadiene polymer; working the mix to effect softening of the butadiene polymer by the halogen-bearing resin-hardening agent to improve the plasticity of the butadiene polymer for mechanical assimilation throughout of the abrasive grain; shaping the mix to give it the desired configuration of abrasive article; and by heat treatment of the shaped mix, vulcanizing the butadiene polymer and reacting the resin polymer at the amino groups thereof with said halogen-bearing agent.

10. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising the copolymer of butadiene with acrylic nitrile, a vulcanizing agent therefor, a resin polymer having amino groups, and a halogen-bearing resin-hardening and copolymer-plasticizing agent in which the halide is selected from the group consisting of chlorine, bromine and iodine, the butadiene copolymer being vulcanized in reaction with the vulcanizing agent and the resin polymer being hardened by reaction at the amino groups thereof with the halogen-bearing hardening agent.

11. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising the copolymer of butadiene with methyl acrylic nitrile, a vulcanizing agent therefor, a resin polymer having amino groups, and a halogen-bearing resin-hardening and copolymer-plasticizing agent in which the halide is selected from the group consisting of chlorine, bromine and iodine, the butadiene copolymer being vulcanized in reaction with the vulcanizing agent and the resin polymer being hardened by reaction at the amino groups thereof with the halogen-bearing hardening agent.

12. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising the copolymer of butadiene with styrene; a vulcanizing agent therefor, a resin polymer having amino groups, and a halogen-bearing resin-hardening and copolymer-plasticizing agent in which the halide is selected from the group consisting of chlorine, bromine and iodine, the butadiene copolymer being vulcanized by reacting with the vulcanizing agent and the resin polymer being hardened by reaction at the amino groups thereof with the halogen-bearing hardening agent.

13. The steps in the method of making an abrasive article which comprise working up on mill rolls a vulcanizable butadiene polymer in admixture with a potentially reactive resin polymer having amino groups therein by the aid of a liquid

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halogen-bearing resin-hardening agent in which the halide is selected from the group consisting of chlorine, bromine and iodine and which is reactive at elevated temperatures with the resin polymer at the amino groups thereof and is substantially non-reactive therewith at mill-roll working temperatures whereby the liquid agent contributes to the softening and plasticizing of the butadiene polymer to improve its receptivity of abrasive grain; admixing abrasive grain therewith for substantially uniform distribution thereof throughout; shaping the resultant substantially plastic abrasive mix; and by heat treatment of the shaped mix reacting the halogen-bearing agent with the potentially reactive resin polymer to harden the latter, and vulcanize the butadiene polymer.

14. An abrasive article according to claim 4 in which the said halogen-bearing agent is tri-glycol dichloride.

15. An abrasive article according to claim 4 in which the said halogen-bearing agent is di-2-chlorethyl formal.

16. An abrasive article according to claim 4 in which the said halogen-bearing agent is di-2-chlorethyl phthalate.

17. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising butadiene polymer, a vulcanizing agent therefor, aminated phenol formaldehyde resin

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in potentially reactive form, and tri-glycol dichloride as a plasticizing agent for the butadiene polymer and as a hardening agent for the resin, the butadiene polymer being vulcanized by reaction with the vulcanizing agent and the resin being hardened by reaction at the amino groups thereof with the tri-glycol dichloride.

18. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising butadiene polymer, a vulcanizing agent therefor, aminated phenol formaldehyde resin in potentially reactive form, and di-2-chlorethyl formal as a plasticizing agent for the butadiene polymer and as a hardening agent for the resin, the butadiene polymer being vulcanized by reaction with the vulcanizing agent and the resin being hardened by reaction at the amino groups thereof with the di-2-chlorethyl formal.

19. An abrasive article comprising abrasive grain bonded by a bond that comprises the reaction product, under heat treatment, of a mix comprising butadiene polymer, a vulcanizing agent therefor, aminated phenol formaldehyde resin in potentially reactive form, and di-2-chlorethyl phthalate as a plasticizing agent for the resin, the butadiene polymer being vulcanized by reaction with the vulcanizing agent and the resin being hardened by reaction at the amino groups thereof with the di-2-chlorethyl phthalate.

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