This invention pertains to a moldable, self-adherent, and durable coating composition and to a method for preparing the same. For illustrative purposes, the invention as a whole is particularly described as utilized in connection with the heeling and soling of shoes although it is obviously not limited thereto. This application is a continuation-in-part of application, Serial No. 58,361, filed November 4, 1948, now abandoned.

In addition to leather, many compositions have been proposed for use in the soling of shoes. These compositions have usually employed rubber or other synthetic materials, or mixtures of these as base materials. To these base compositions different types of fillers have also been added in varying concentrations. The type and quantity of filler used is largely dependent on the wearability and flexibility ultimately desired in the finished sole.

These compositions, however, are manufactured in sheet or board form and must be cut to size by the skilled shoe worker or repairman when repairing shoes. In some instances, these soles are stamped or pressed in different shoe sole and heel sizes at the plant thus relieving the worker of some waste and the extended cutting step.

Before the sole, either composition or leather, is placed on the shoe bottom, a binder is generally applied to the shoe bottom or sole to secure the two together. This binder may take the form of an adhesive and its use may require the application of heat and pressure to insure a good bond. Where the sole is of a thermo-plastic nature, the step of vulcanization may be required. Furthermore, where vulcanization or gluing is not suitable, it is usual to rivet, nail, sew, or by similar mechanical means secure the sole to the shoe bottom.

Thus, it is apparent that in the process of soling shoes there has existed for some time the step of cutting or stamping, etc., the sole material before it can be placed on the shoe bottom requiring skilled workmanship with the further requirement of an additional material, and very possibly an additional step being needed to secure the sole to the shoe bottom.

It is, therefore, an object of this invention to provide a moldable, self-adherent and durable coating composition.

It is another object of this invention to provide a shoe sole composition that may be shaped without cutting or stamping and may be secured to shoe bottoms without the need of adhesives, heat, pressure, or mechanical attaching means.

It is still another object of this invention to provide a method for making a shoe sole composition characterized by the fact that it can be directly applied to shoe bottoms and shaped without cutting or stamping and without the necessity of employing adhesives, heat, pressure, or mechanical securing means.

It is yet another object of this invention to provide shoes with heels and soles of a strong, wear-resistant and self-adherent composition of matter.

It is a further object of this invention to provide a method for applying a shoe sole composition to a shoe bottom without the necessity of cutting or stamping the material or of applying heat, pressure, adhesives, or mechanical securing means.

It has now been found that polymerized chloro-2-butadiene-1,3 of the "AC" type, when milled for a determinable period of time breaks down and can be readily dissolved in a volatile, hydrocarbon-type solvent and, on the addition of a filler, and preferably a resin, which are thoroughly mixed therewith, forms a moldable, shoe sole composition. This semi-plastic composition can then be applied by unskilled persons by means of a spatula to a cleaned, dry and roughened shoe bottom, and on drying by the evaporation of the solvent forms a self-adherent, tough, long-wearing shoe sole.

This polymerized chloro-2-butadiene-1,3 of the "AC" type as manufactured by the Du Pont Company, hereinafter called "neoprene," should conform to A. S. T. M. requirements as shown in their specification entitled "Tentative method of test for plasticity and recovery of rubber and rubber-like materials by the parallel plate plastometer," A. S. T. M.—D—926—47—T, with plasticity numbers (readings made in millimeters) of 302 to 377 and recovery numbers of 38 to 53 at 80° C. and 3 minutes. The neoprene has a specific gravity of about 1.23, and it can contain traces of iron compounds, soap or antioxidants such as are well known to those skilled in the art.

If about 1½ pounds of this neoprene are milled on a two roll, water-cooled, 12 inch rubber mill for less than about 10 minutes, however, or not at all, the neoprene swells in the hydrocarbon solvent and will not readily go into solution to form a composition that can be used for soles. On the other hand, if the neoprene is milled for over 30 minutes, it has been found that the resulting composition has become too soft and sticky, and due to too much flow it lacks the quality of retaining its shape when applied to shoe bottoms and on evaporation of the solvent. A milling
period of from about 10 to about 30 minutes has been found to give very satisfactory results. The shoe sole composition made with this milled neo-
prene after being applied to the shoe bottom and an evaporation of the solvent is adhesive and does not exhibit any tendency to cold flow. Ex-
cellent shoe sole compositions have been obtained when using neoprene milled for about twenty
minutes. The plasticity numbers of this material and neoprene should be from about 280 to 350 at 80 °C.
Although it has been shown above that the plasticity numbers for the neoprene before milling are from about 302 to about 377, the unmilled neoprene lacks adhesive properties, its molec-
ular structure is such that it will gel in the solvent, or it will not properly go into solution until it has been milled for about 10 to 30 minutes. Fur-
thermore, it is not necessary to use milled neo-
prene of one plasticity number. For example, one-half of the milled neoprene used in the com-
position can have a plasticity number of about 330 and the other half can have a plasticity num-
ber of about 280.

The milling can be performed in other types of rubber milling machines than that disclosed
above and where the rollers are very closely posi-
tioned together and operated at different speeds so that the rubber is crushed and rubbed rather
than rolled around. It is, of course, obvious to
those skilled in the art that when milling on other
machines, the time will vary somewhat from the
above depending on the size of the rubber mill, the
quantity of neoprene, the speed of the rolls, the
temperature, the spacing between the rolls, etc.
For example, it will take from 40 to 90 minutes to
obtain sufficient milling on a 60 inch mill, to
result in a milled neoprene having the above desire-
able properties as represented by its plasticity
numbers of from 320 to 355. From 20 to 30 min-
utes is required on a 30 inch mill. A “refiner,” i.e., a mill where one roll is usually larger than
the other and which is generally used in the rub-
ber reclaiming industry, can likewise be employed
to mill the neoprene.

After milling, the neoprene is dissolved in a suitable hydrocarbon solvent. This can be con-
veniently accomplished by adding the solvent to the milled neoprene in a cement churn, or dough
or paddle-type mixer. The milled neoprene can be
grate, chopped, ground or otherwise finely
divided in order to facilitate dissolving it in the
solution. This can be obtained by first freezing or chilling the neoprene followed by frictional
disintegration, etc. The time required to mix and
dissolve the neoprene will vary from about two to
about five hours depending on the quantities of
neoprene and solvent used. About three hours
mixing time at room temperature is usually suffi-
cient to dissolve the milled neoprene.

It has been found that from about 20 to about
28% by weight of the milled neoprene in the hy-
drocarbon solvent results in an excellent base
composition. Expressed in another way, there
is a range from 100 parts by weight of the dry milled
neoprene to from 250 to 400 parts by weight of the
hydrocarbon solvent. A solvent solution which
provides good results is prepared by mixing from
40 to 60 parts by volume of toluene with from 60
to 70 parts by volume of gasoline. The primary
function of the gasoline is to dissolve the milled
neoprene while the primary function of the gaso-
line is to promote evaporation. Benzene or xy-
lene may be substituted for the toluene, and in
place of the gasoline, heptane, hexane, or pen-
tane can be used. It is, of course, obvious to those
skilled in the art that many other hydrocarbon
solvent can be utilized in this invention besides
the one illustrated.

While this process provides a shoe sole composi-
tion that is applied to shoes without the necessity of vulcanizing, heating, using pressure, adhesives
or mechanical securing means and which, of it-
self, is strongly adherent to the shoe bottom, cer-
tain special resinous materials may be added to
the composition, if found desirable, to improve
somewhat the initial tack and bond strength of the resultion composition. These materials in-
clude wood resin derivatives (such as hydrogen-
ated methyl abietate), resin ester derivatives such
as styrhelene ester (polyhydric alcohol ester of
hydrogenated resin) or ester gum (glycerol ester
of resin), phenol-formaldehyde resins, resorcin-
ol-formaldehyde resins, coumarone - indene
resins, etc. They are generally added to the neo-
prene solution prior to the addition of the filler
in the proportion of about 1 to 10 parts by weight
of the resin to about 100 parts by weight of the dry neoprene.

When the milled neoprene has completely dis-
solved in the solvent, and after the resins mate-
rials have been added thereto, a filler is then
added and mixed in with the solution. Instead of
adding the filler to the neoprene solution, it also
can be added to the neoprene while it is being
milled on the rubber mill, and, thus, the time of
preparation of the shoe sole composition can be
readily reduced. The ratio of filler to neoprene is
from 30 to 70 parts by weight of the dry neoprene
by weight of dry neoprene. If the composition
contains more than 70 parts of filler, it is too
viscous to handle readily and adherence is poor
while less than 30 parts of filler results in less
strength, poor wearing qualities, and slow drying.

At least 40% by weight of this filler must be
fibrous in order to obtain satisfactory product.
The fibrous filler aids in shaping the sole when
using a spatula or similar tool, improves the wear-
ability of the resulting sole, and promotes evapo-
ration of the solvents. An example of a suitable
fibrous filler is leather fiber; or, a mixture of
leather fibers and cotton fibers may be advantage-
ously used, the cotton fibers having lengths of
from 0.090 inch to 0.25 inch. The cotton and
leather fibers can be mixed in any proportion,
although it is preferred to mix them in the ratio
of from 25 to 75 parts by weight of leather to
from about 70 to 25 parts by weight of cotton.
Other suitable organic and mineral fillers, having
good abrasive and wear qualities can be added in
amounts up to 60% by weight of the total filler
material in the neoprene solution. These addi-
tional fillers can be added singly or mixed together
and include rock wool, clay, hydrated calcium
silicate, carbon black, metallic particles, cellulose
flock, wood flour, ground cork, nut shell meal or
flour, leather dust, leather blocks or particles,
hard rubber dust, Vinylvle or styrene and other
synthetic or resinous dusts, wood fiber and syn-
thetic yarn fiber (viscose rayon or cellulose ace-
tate).

At the time the filler is added to the solution in
the mixer, a small amount of dispersing agent can
also be added to reduce the overall mixing time.
From about 1/4 to about 1/2 part by weight of light-
per 100 parts by weight of the dry neoprene is an
excellent material for this purpose.

The neoprene in the composition can liberate small amounts of hydrochloric acid during stor-
age or while in service with some deterioration of
cellulose and other materials. It is there-
fore, desirable in some cases to add acid acceptors to the composition. For this purpose about four parts of calcined magnesia and about five parts of zinc oxide per 100 parts of the dry neoprene can be used.

To change the color of the composition small amounts of organic and inorganic dyes such as are well known to those skilled in the art may likewise be added to the composition.

The shoe sole composition can now be readily applied by unskilled persons at home to a shoe bottom which has been roughened, cleaned and dried. It is preferred to first rub some of the composition over the entire surface of the prepared shoe bottom. This thin layer does not have to thoroughly dry. Then a spatula, dipped in water to prevent the adherence of the composition to it, can be used to apply a thick coating of the composition to the shoe bottom. In place of a spatula, it is obvious that a knife or other simple tool can be employed. As soon as a skin coat has formed on the surface of the thick coating, the layer can be brought by means of the spatula to conform to the configuration of the shoe bottom. Alternatively, the coating can be shaped before the skin coat forms by using the spatula which has been dipped in water. After applying the composition sole, the shoes are placed on their soles up in order to dry. Thick coats on soles take about 48 hours to dry. Thin coats take about 24 hours. Since a thick coating applied all at once will contract slightly on thorough drying and also tend to be less dense, it is desirable to apply the shoe sole composition in such a manner that, of which is molded with the spatula and allowed to form a skin coat or a dry somewhat until the desired thickness has been achieved. For example, a coating of the composition ¼ inch thick will on drying be about ¼ inch to ½ inch thick. By applying successive coats a substantially non-porous, water-proof, adherent sole of the desired shape and dimensions can be obtained.

This neoprene shoe sole composition containing a volatile solvent and a filler has excellent keeping qualities if suitably packaged so that the solubility of the plasticizer and rubber does not need to be used immediately after compounding as no polymerization or other adverse reactions set in. Packaged in commercially available screw cap containers or other sealable containers having metal surfaces of tin, aluminum or glass which do not cause deterioration of the neoprene, it will maintain its semiplastic condition for extended periods of time and can be used as required to cover shoe bottoms. Where iron containers are used, the composition may discolor over a period of time. The introduction of certain ingredients like zinc oxide or calcium silicate in an amount of about 5 parts per 100 parts of dry neoprene will serve to prevent this discoloration. Magnesium oxide in an amount up to four parts per 100 parts of dry neoprene will also serve to improve the stability of the composition.

The following example will serve to illustrate the invention with more particularity:

35 parts by weight (about 1.5 pounds) of neoprene was milled for 20 minutes on a 6 x 12 inch, 2-roll rubber mill having a clearance between the rolls of approximately 0.020". The speed of the front roll was 18 R. P. M. While the speed of the rear roll was 26 R. P. M. The gear ratio was thus about 1.4. The rolls were cooled by circulating water through them.

After milling, the neoprene was removed from the mill and dissolved in 75 parts by weight of a hydrocarbon solvent composed of 40% of toluene and 60% of gasoline. To this solution was then added 15 parts by weight of leather fibers and 1.5 parts by weight of camphorone-iodene resin, both based on the dry weight of the neoprene. The mix was then thoroughly stirred and the resulting, semi-solid, or plastic mass was applied by means of a spatula to a clean, dry, roughened shoe bottom to form a sole about ½" thick without the use of any heat, pressure, adhesives, etc.

After an air drying period of about 48 hours, the composition shoe sole was tested and its adherence and wearability found to be excellent.

The precise chemical or physical reactions which occur in this novel process, to result in such a tightly adherent shoe sole composition, are not clearly understood. It is thought, however, that by milling polymerized chloro-2-butylenne-1,3 in a two-roll rubber mill, having rollers approximately 0.030" apart, the neoprene is changed in molecular structure and will readily dissolve in the solvent carrier. Unmilled neoprene will not form gels in the solvent and will not readily go into solution nor produce a composition having adhesive qualities, whereas milling appears to destroy the gel structure resulting in a material which will go into solution and form a composition having excellent adhesive properties.

Furthermore, milling changes the viscosity of the solution of neoprene. For example, a solution of an unmilled neoprene having a plasticity number of 500 will have a viscosity of 1 to 1½ minutes while a solution of "milled" neoprene of the same plasticity will have a viscosity of ½ to ¾ minute as shown by the Modified Gardner-Hold test. The dissolution of neoprene in the solvent also seems to facilitate, on the addition of the fibrous filler, an intimate association, dispersion or mixture. These finely divided particles on drying appear to form a strong neoprene-to-fiber bond giving exceptionally good tensile strength. Furthermore, since the neoprene appears to have been reduced in molecular size or changed in molecular structure, it readily penetrates the fibrous leather surface of the shoe bottom permitting great adherence of the neoprene with the shoe bottom. It is also believed that the increased density of the mass resulting from this intimate association of fine particles renders the composition hard and durable as well as adherent and substantially non-porous. Such porosity as may exist in the dried coating is in the form of microscopic air pockets which are probably unconnected, for the dried coating is actually not only water-resistant but water-proof.

This neoprene shoe sole composition can be applied to heels as well as to shoe bottoms. It will also adhere to the soles of shoes where the sole is firmly attached to the shoe bottom and is in good condition, thereby, eliminating the need of removing the old shoe sole. It also adheres readily to previous soles of the composition. It may also be used to cover the sides or uppers of the shoe to render them water-proof. Likewise, the soling composition can be employed to coat other composition soles or rubber soles as found in slippers, boots, rubbers, galoshes, etc. By brushing, cleaning, and drying the bottom, the soling composition is easily placed thereon and adheres as satisfactorily as when placed on leather bottoms. In the case of rubber articles, it is believed that the solvent in the soling composition
2,800.8 partially dissolves the rubber on the surface of the galosh or rubber forming a strong bond at the interface between the old rubber surface and the new composition sole.

To determine the flexibility and resistance to abrasion of the shoe sole composition, samples were prepared having a weight and density approximately that of leather. Several thin dried sheets of the composition about ⅛" to ⅜" thick, which were slightly porous, were placed together, heated to 150° F. and pressed together in a press operating at pressure of 500 lbs. sq. in. The resulting samples in the form of strips 1" x 6" x ¼" were compared with oak tan leather strips of the same dimensions in a Ross Flexer. Both the leather and the composition sole material would take from 10,000 to 30,000 flexes before a 0.5 inch cracking was observed. The abrasion resistance was determined by ASTM D—394—37, method B. The National Bureau of Standards type of abrader was used. 0.1 inch of leather was removed in from 100 to 250 revolutions while 0.1 inch of the sample of composition material was removed in from 100 to 200 revolutions.

In summary, it will be apparent that there has been disclosed a novel method of preparing a shoe sole composition which will satisfactorily adhere to shoe bottoms without the necessity of using adhesives, heat, pressure, etc. This composition has been made possible by the discovery that, if neoprene of a certain special type, as hereinbefore described, is milled for a period of about 10 minutes but not more than about 30 minutes on a 12" mill, it has been placed in a very excellent physical condition for ultimately forming a composition with a fibrous filler material that will suitably adhere to shoe bottoms. This invention, thus, provides a novel, easy and inexpensive process for making or repairing shoe bottoms, utilizing a moldable and self-adherent composition, and eliminating the former steps of cutting or prestamping soles before applying them to shoe bottoms, as well as the need for binding materials or operations or for skilled workmanship.

It is to be understood that while the invention has been described with particular emphasis on the healing and soiling of shoes, it is quite obvious that the composition and its method of application described herein have a great many other useful applications. For example, the novel composition can find many uses where a tough, moldable, and self-adherent coating material is required. It can readily be used to repair leather goods such as suitcases and briefcases or canvas articles such as tents and awnings, etc.

What is claimed is:

1. A coating composition for spreading with a spatula or the like and having good adhesive and drying properties, and flexibility together with high resistance to cold-flow and wear in the dry condition, comprising 100 parts milled poly-chloro-2-butadiene 1,3 substantially insoluble in hydrocarbon solvent prior to milling and alone having optimum stickiness and a plasticity within the approximate ASTM number range of 280 to 355 based on a temperature of 80° C. and said polymer being dissolved in about 250 to 400 parts by weight of a hydrocarbon solvent, 1 to 10 parts of an initial tack and bond strength improving resin of the group consisting of wood resin derivatives, phenol-formaldehyde resins and coumarone-indene resin, and about 30 to 70 parts by weight filler of which at least about 40% is made up of fibers.

2. A coating composition as defined in claim 1 wherein said hydrocarbon solvent consists of from 40 to 60 parts by volume of toluene and from 60 to 40 parts by volume of gasoline.

3. The coating composition of claim 1 wherein said filler is made up of at least 40% leather fibers.

4. A coating composition for spreading with a spatula or the like and having good adhesive and drying properties, and flexibility together with high resistance to cold-flow and wear in the dry condition, comprising 25 parts milled poly-chloro-2-butadiene 1,3 substantially insoluble in hydrocarbon solvent prior to milling and alone having optimum stickiness and a plasticity within the approximate ASTM number range of 280 to 355 based on a temperature of 80° C. and said polymer being dissolved in about 75 parts by weight of a hydrocarbon solvent, about 1.5 parts by weight of a coumarone-indene resin and about 18 parts by weight of leather fibers.

CECIL F. BACKUS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,640,946</td>
<td>Loomis et al.</td>
<td>Aug. 30, 1927</td>
</tr>
<tr>
<td>1,766,907</td>
<td>Geppert</td>
<td>Dec. 30, 1930</td>
</tr>
<tr>
<td>2,163,609</td>
<td>MacDonald</td>
<td>June 27, 1959</td>
</tr>
<tr>
<td>2,332,000</td>
<td>Murray</td>
<td>Oct. 19, 1943</td>
</tr>
<tr>
<td>2,367,481</td>
<td>Burger</td>
<td>Jan. 16, 1945</td>
</tr>
<tr>
<td>2,376,854</td>
<td>Saunders</td>
<td>May 22, 1945</td>
</tr>
<tr>
<td>2,431,001</td>
<td>Sullivan</td>
<td>Nov. 18, 1947</td>
</tr>
</tbody>
</table>

OTHER REFERENCES