Oct. 12, 1943. J. W. RAYNOLDS ET AL 2,331,728

CONTAINER CLOSURE

Filed May 14, 1942

Fig. 1.

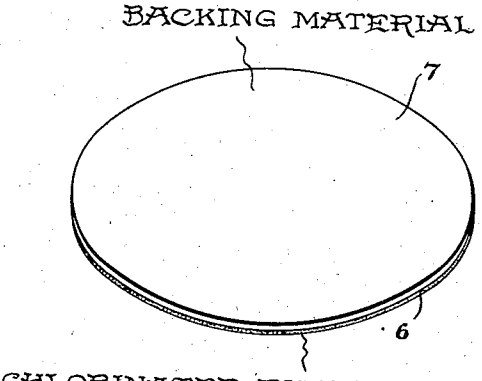
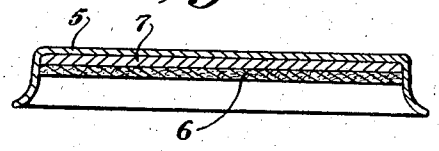


Fig. 2.



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Patented Oct. 12, 1943 2,331,728

UNITED STATES PATENT OFFICE

2,331,728

CONTAINER CLOSURE

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Application May 14, 1942, Serial No. 443,010

3 Claims. (Cl. 215—40)

This invention or discovery relates to container closures; and it comprises an improved closure top for containers for foods, beverages, drugs, cosmetics and the like, said closure top being provided on an inner surface with a layer or film of chlorinated rubber hydrochloride which advantageously contains from 42 per cent to 52 per cent chlorine, said layer being advantageously applied to a separable liner of paper, pulp board, cork sheeting, or the like, which may have gasketing functions; and it comprises liners for such closures; all as more fully hereinafter set forth and as claimed.

Foods, drugs, cosmetics and other commodities are often packaged in bottles, jars and like containers having removable tops or closures. Such closures are often provided with lugs or threads adapted to engage the neck of the bottle or jar, and are usually made of metal or of molded plastic material. In practically all cases, the color, taste and odor of materials packaged in containers of this type are important, and it is therefore frequently necessary to protect the closure and the contents of the container from contact with each other. Many varnish coatings and coatings of related composition for caps and cap-liners have therefore been proposed.

Coatings of rubber chloride are frequently useful in the protection of packaged materials from contact with container closures, and rubber chloride has many virtues for this purpose, owing to its chemical inertness. It is not affected by acids, alkalies or alcohols, or by most of the materials packaged in containers of this type. Rubber chloride is, however, soluble to a certain extent in the fatty oils, and conversely it takes up fatty oils. A film or lining of rubber chloride is not grease-proof and caps protected by it are not of universal applicability. Many foods, drugs and cosmetics contain fats or greasy materials.

There are a number of rubber chlorides or chlorinated rubbers known, but all have the drawback of susceptibility to grease. These compounds are products resulting from the reaction of chlorine (usually in the gaseous state) and rubber (usually in solution). The most stable products contain about 64 to 68 per cent of chlorine and are thought to have compositions corresponding to the formulas $C_{10}H_{13}Cl_7$ or $C_{10}H_{12}Cl_8$. In such compositions, four chlorine atoms have been combined by addition at the double bonds of the caoutchouc, and three or four chlorine atoms have been entered by substitution. The reactions which produce these compounds are conveniently carried out in carbon tetrachloride or other chlorine-resistant solvents, and it appears that the addition and substitution of chlorine progress to completion more or less simultaneously. Various modifications of the process of chlorinating rubber have been disclosed heretofore. Useful procedures are described in U. S. Patent 2,148,830 to North and in a copending application of Raynolds, Serial No. 245,293.

As used herein, the terms "rubber chloride" and "chlorinated rubber" refer to chemical compounds of the class discussed hereinabove, which characteristically have a combined chlorine content of 64 to 68 per cent; part of the chlorine saturating double bonds and part being substituent.

A somewhat similar, or at least related, class of compounds are produced by the reaction of rubber and hydrogen chloride in the absence of free chlorine. These products, which are known as rubber hydrochlorides, are formed by reaction of gaseous or liquid HCl with rubber until the double bonds in the rubber have been satisfied. The product of this reaction is theoretically rubber di-hydrochloride, having a composition corresponding to the formula $C_{10}H_{18}Cl_2$. This theoretical composition corresponds to a chlorine content of 34.8 per cent, but in practice, it is seldom possible to obtain products containing more than 31 to 32 per cent of chlorine.

Rubber hydrochloride films are useful as linings for certain foods, drugs, cosmetics and other commodities, and the composition is quite resistant to acids, alkalies, alcohols and most of the materials which are packaged. Rubber hydrochloride is also quite resistant to vegetable oils, being superior to rubber chloride in this respect.

There are, however, several undesirable factors which impair the utility of rubber hydrochloride for the coating of container closures. One of these is the excessive thermoplasticity which is a general characteristic of rubber hydrochlorides. Many food products and cosmetic preparations are packaged and sealed hot; and others are packed cold, and then heated to pasteurize or sterilize the packaged material. When used in such processes, rubber hydrochloride films of the characteristic chlorine content (below about 32 per cent) soften; and then as the container and its contents cool, the vacuum created in the container causes the rubber hydrochloride to bulge and become permanently distended, thus destroying its usefulness and appearance. The

thermoplasticity of rubber hydrochloride also frequently causes liners or closures coated with this material to adhere to the mouth of the jar or other container with which they are employed. Several other disadvantages also result from the excessive plasticity and stickiness of this material when hot.

Another unfavorable characteristic of rubber hydrochloride is its low solubility. It is only soluble to a small extent in the solvents which are normally desirable for coating purposes, such as benzol and toluol. The symmetrical type of rubber hydrochloride is only soluble to the extent of some 2 or 3 per cent, and the asymmetrical type of rubber hydrochloride, although somewhat more soluble, will not form solutions having a solid concentration above about 7 per cent. Such solutions form very thin films on drying, and are not satisfactory for application as varnish coatings to paper and other materials. Varnishes which are economical for use in such applications should contain more than 20 percent, and advantageously between 25 and 30 percent, of solids in a solution having a viscosity between 1500 cps. and 2500 cps. Rubber hydrochloride cannot be made into solutions or varnishes of this character.

As a result of this difficulty, it has been necessary heretofore to resort to some other method of applying rubber hydrochloride films and coatings. For example, films can be formed from benzol solutions of rubber hydrochloride containing up to 7 per cent solids by the process disclosed in Patent No. 2,078,526. The separate film of rubber hydrochloride may then be coated on one side with an adhesive and cemented to paper or pulp board or the like to form closure lining material. Considerable difficulty has been encountered in producing a permanent bond between the rubber hydrochloride film and the paper carrier, however, and for this and other reasons, the use of these rubber hydrochloride films in closure liners is not economical.

Rubber hydrochloride can be treated with chlorine gas to yield products having considerably increased chlorine contents. The reaction involved is essentially a substitution reaction, and the HCl which is added in forming the rubber hydrochloride is not easily displaced. Products of this reaction apparently have compositions corresponding to the formulas $C_{10}H_{17}Cl_3$ (containing 43.7 per cent chlorine) and $C_{10}H_{16}Cl_4$ (containing 51.04 per cent chlorine). Such products are known as chlorinated rubber hydrochlorides, and their existence has been disclosed heretofore.

We have found that certain suitably prepared chlorinated rubber hydrochlorides containing from 42 to 52 per cent of combined chlorine are eminently suitable for use in container closures. These products, to be hereinafter described more in detail, are soluble in concentrations up to 25 per cent or more in benzol or toluol and thus are suitable for application as a varnish. The resulting coating possesses sufficient thickness for closure liners and the like. The resulting films are free from the objections noted hereinabove. We have also found that paper coated with one or two coats of this chlorinated rubber hydrochloride varnish has highly desirable properties for use as a closure lining or gasket. Such varnish coatings or films are unaffected by acids, alcohols, mineral oils and alkalies, or by cottonseed oil and other vegetable oils. In addition, a coating of this chlorinated rubber hydrochloride has a very low moisture permeability as compared with all other types of closure lining materials.

Still further, the chlorinated rubber hydrochloride does not have the excessive thermoplasticity which, as noted, is an undesirable characteristic of ordinary rubber hydrochloride. The thermoplasticity of rubber hydrochloride is substantially reduced when the product is chlorinated, and when a chlorine content of about 43.7 per cent chlorine is reached, the chlorinated rubber hydrochloride is quite satisfactory for use on hot packs. It does not bulge or deform when the packaged material is cooled, and does not stick to the mouth of a container. The thermoplasticity is still further reduced as the chlorine content is increased. In these respects, the chlorinated rubber hydrochloride films or coatings are decidedly superior to rubber hydrochloride films or coatings for use on container closures or closure liners.

A further advantage of the foregoing chlorinated rubber hydrochlorides containing about 43.7 per cent to 51.04 per cent chorine is their flexibility. Such chlorinated rubber hydrochlorides do not require the addition of plasticizers before application to paper, etc., in the production of closure liners. Their flexibility is adequate for most purposes without the use of plasticizers. The moderate thermoplasticity of this material and its normal flexibility result in the production of coatings on paper and other supporting materials which readily conform to the mouth or finish of the container with which they are used, and thus make an effective seal when the closure is in place.

The chlorinated rubber hydrochloride products employed in accordance with the present invention are limited to a specific range of chlorine content and most advantageously produced in accordance with the process disclosed in the copending U. S. application Serial No. 332,115, filed April 27, 1940. These products must not be confused with the hydrochlorinated rubber chlorides which, as is well known, are a fundamentally different class of compounds, formed by first treating rubber with hydrogen chloride and later with chlorine. This reaction produces a totally different kind of chemical composition having properties unrelated to those of the chlorinated rubber hydrochloride herein employed.

Yet, more specifically, the present materials are distinguished from conventional materials formed by ordinary hydrochlorination of rubber followed by treatment with chlorine. Thus, as pointed out above, conventional hydrochlorination to produce a symmetrical rubber hydrochloride seldom results in a product containing more than 30 per cent chlorine. Chlorination of this product even under the most favorable temperature conditions results in a reaction efficiency which is extremely poor. Large excesses of chlorine have been hitherto found necessary and it has been quite unusual to obtain products containing more than 39 or 40 per cent fixed chlorine. The resultant products have had very poor solubility in conventional solvents, have been characterized by undesirable instability and appearance and are generally unsuited for the purposes of the present invention. In accordance with the present invention, however, the chlorinated rubber hydrochlorides employed not only possess a higher combined chlorine content within the range of 40 to 50 per cent, but have im-

proved properties indicating the possibility of a fundamental difference in chemical structure. Such materials have good solubility in the foregoing commercial solvents, possess improved stability, and are formed as clear solutions.

The details of the preferred method of making these compounds are disclosed in the aforesaid copending application Serial No. 332,115 and reference is accordingly made to this specification for full and complete disclosure of the process. In general, this process involves the chlorination of a suitably prepared rubber hydrochloride solution or dispersion under the influence of ultraviolet light advantageously within the wave length range of from 2800A to 3600 A. Ultraviolet radiation results in a better and more efficient absorption of chlorine, a more thorough and uniform chlorination, and products of higher chlorine content.

In general, therefore, a rubber hydrochloride produced as above and having, for example, a combined chlorine content of about 30 per cent, is chlorinated under the influence of ultraviolet light within the above range of wave length to a fixed chlorine content of 42 to 52 per cent. Chlorination proceeds rapidly, and efficiency of utilization of the chlorine is quite high.

Yet more specifically, the reactions are preferably carried out in the presence of a suitable solvent. Thus the rubber is preferably originally prepared for hydrochlorination by dissolving it in benzene. The resulting cement is dehydrated and the anhydrous product subjected to contact with dry hydrogen chloride gas at a low temperature between 5 and 25° C. for a 24 hour period. The resultant hydrochlorinated product containing about 31 per cent fixed chlorine is then treated with gaseous chlorine at a temperature above about 80° C. and in a vessel providing for continuous circulation of the fluid past a quartz window opposite which is disposed an ultraviolet light. Chlorination to a final chlorine containing above 42 per cent normally does not require more than 2 hours under the stated conditions. The product is then blown to remove residual gases and the solid chlorinated hydrochloride recovered from the solution in any convenient manner.

While other methods may be employed in the production of the present materials it is to be understood that the foregoing illustrates a preferred method of producing materials of optimum properties and considered highly superior and advantageous in carrying out the present invention.

It is particularly important to note that for the purposes of the present invention chlorinated rubber hydrochlorides having a chlorine content substantially less than 43.7 per cent are generally too thermoplastic and characterized by the objectionable properties of ordinary rubber hydrochloride. On the other hand, when the chlorine content of the product is increased substantially above 51 per cent there is an accompanying increase in the brittleness, rendering necessary the addition of plasticizers and accompanying impairment of resistance to vegetable oils or other ingredients of package materials. In short, it has been discovered that those products occurring between the foregoing limits of chlorine content and more broadly within the range of 42 to 52 per cent encompass a field highly suitable and desirable for use in container closures.

It should be noted that products of similar chlorine content can be prepared by reacting rubber with gaseous chlorine in the usual manner employed in the manufacture of chlorinated rubber. However, such products do not exhibit satisfactory resistance to numerous reagents, and they are inferior to the rubber chlorides described hereinabove containing 64 per cent or more of chlorine. In order to obtain the most desirable properties, it is necessary to prepare rubber hydrochloride first, and then to chlorinate the hydrochloride to a total chlorine content between 42 per cent and 52 per cent. The chlorinated rubber hydrochlorides of this chlorine content are free from the unfavorable characteristics of both rubber hydrochloride and rubber chloride. It thus appears that the addition to ordinary rubber hydrochlride of about 10 to 20 per cent of substituted chlorine eliminates the undesirable characteristics of the hydrochloride (low solubility and excessive thermoplasticity) without impairing its grease-resistance or other desirable properties.

These chlorinated rubber hydrochlorides form coatings which are colorless, tasteless, odorless and non-toxic. The coatings may be pigmented if desired, titanium di-oxide being a useful pigment for the production of white coatings. Other pigments may, of course, be used when other colors are desired.

As a specific illustrative example of the present invention, a chlorinated rubber hydrochloride produced in accordance with the process described in copending application Serial No. 332,-115, containing 47.7 per cent of chlorine is dissolved in toluol to form a solution containing 23 per cent solids. The solution has a viscosity of 2500 cps. at 25° C. and is entirely satisfactory for varnish coating or roller coat application. As a base for the closure liner employed with this coating, a paper is selected having sufficient density to minimize permeation by the coating solution or the solvent. Numerous such papers having satisfactory properties in this respect are available and pulp board or cork sheeting are also satisfactory, preferably if first treated with a suitable sizing or sealing coating.

The chlorinated rubber hydrochloride solution or varnish is applied to the selected paper by roller coating, although it could equally well be applied by a knife or spreader, or by spraying or other suitable means. The thus coated paper is dried in an oven at a temperature of 220° F. for 10 minutes. It will be understood that the time and temperature of baking may be varied in accordance with the type of oven employed and the solvent used resin solution. Multiple coatings are readily applied by repeating the process, if desired.

The resulting coated paper possesses a dry film of chlorinated rubber hydrochloride having a thickness of 0.001 inch. This film tested for moisture permeability by the standard moisture vapor transmission method of the New York Paint and Varnish Production Club, using standard Payne cups, showed a specific permeability of 0.0669 mg. at 900° F. and 0 per cent relative humidity. As a comparison, normal rubber hydrochloride sold for closure lining material showed a specific permeability of 0.120 mg. at 100° F. and 0 per cent relative humidity in this test. A rubber chloride-vinyl acetate composition disclosed in a copending application of Raynolds, Serial No. 253,861, showed a specific permeability of 0.1225 mg., and a coating of the co-polymer of vinyl chloride and vinyl acetate showed a specific permeability of 0.33 mg., in

both cases at 100° F. and 0 per cent relative humidity, by this test. It is therefore clear that the chlorinated rubber hydrochloride coatings produced in accordance with this invention have extremely low moisture permeability.

As a further test of the coating produced in accordance with our invention, the coated paper was cut into closure liners, which were assembled with metallic closure bodies. Separate glass jars were then filled with each of the following testing materials:

Sodium hydroxide	2
Ammonia Chlorox (sodium hypochlorite)	10
Phosphoric acid	85
Hydrochloric acid	10
Acetic acid and 20% salt brine Milk of magnesia	8
Ethanol	50
Ethanol "Astringosol" Cottonseed oil	95
Hydrogen peroxide	3
Acetic acid Glacial acetic acid Squibb's sun tan oil (contains methyl salicylate)	50
Ferric chloride	10
Sodium carbonate	1
Salt in distilled water	½

The assembled closures having liners coated as described hereinabove were then placed on the jars with the coating exposed to the contents, and the jars were heated to a temperature of 150° F. for 48 hours. At the end of this time, the coatings on the liners were examined and none of them showed any signs of deterioration. Similar results were obtained with the contents heated to 105° for seven days' exposure. Samples were tested by exposure to cottonseed oil for 18 days at 150° F. without any noticeable effect on the coating. Similar results were obtained in testing pigmented coatings.

In addition to the excellent resistance and low moisture permeability of the chlorinated rubber hydrochloride coatings produced in accordance with this invention, they also form products of very attractive appearance. For example, paper coated as described hereinabove is not changed in color by the application of the coating, and when white paper is used, the coated paper has a very clean white appearance. Such coatings, and liners provided with such coatings, are therefore well adapted for use with containers for food products, beverages, cosmetics, drugs and the like.

In commercial operations employing liners of this type, the coated paper or other coated material is run through a stamping mechanism which stamps out liners of any desired diameter. For some special purposes, laminated materials are employed, and these may be made entirely of paper or other cellulosic material, or may include aluminum foil or other material. In any case, the coating produced in accordance with this invention is sufficiently flexible to conform to the container mouth during sealing; and because of its extremely low moisture transmission rate, it insures the retention in the container of volatile ingredients to a greater extent than with other commercial liners now available. A further advantage is that our new closure liner coating material is sufficiently low in cost to compete favorably from an economic standpoint, even with many inferior materials which are now on the market.

Referring to the accompanying drawing, wherein one exemplary embodiment of the invention is disclosed more in detail,

Figure 1 discloses a closure liner, described above; and

Fig. 2 shows the liner associated in operative relation with a conventional type of closure member.

In the drawing, the reference numeral 5 designates the shell of a closure provided with a liner 7 coated with a layer 6 of chlorinated rubber hydro-chloride.

While our coating of chlorinated rubber hydrochloride gives especially advantageous results when applied to liners for container closures, it is also useful in many other applications where resistance to greases, solvents, acids, bases and salts is desired. For example, it may be applied directly to the surface of metal and other articles, including closures. As previously noted, pigments may be included in the coating composition if desired, and are often advantageous in that they reduce the specific permeability of the coating still further. Any compatible pigment may be employed.

This application is a continuation-in-part of U. S. Serial No. 326,803.

What we claim is:

1. In a closure for containers, a substantially insoluble grease-proof film disposed between the inner surface of the closure and the interior of the container and adapted to prevent contact between the closure and the contents of the container, said film consisting principally of chlorinated rubber hydro-chloride containing from 42 per cent to 52 per cent of combined chlorine and being characterized by flexibility, freedom from excessive thermoplasticity, extremely low moisture permeability, and resistance to acids, alkalies, oxidizing agents, salts and esters, including vegetable oils.

2. The closure of claim 1, wherein the said film is applied to a liner provided within the closure body.

3. A liner for container closures comprising a base and a coating applied to said base on the side exposed to the contents of the container, said coating consisting principally of chlorinated rubber hydro-chloride containing from 42 per cent to 52 per cent of combined chlorine and being characterized by flexibility, freedom from excessive thermoplasticity, extremely low moisture permeability, and resistance to acids, alkalies, oxidizing agents, salts and esters, including vegetable oils.

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