Patented Sept. 15, 1953 2,652,182

UNITED STATES PATENT OFFICE

2,652,182

COATED RUBBER STOPPER AND PROCESS FOR PREPARING SAME

Robert R. Umbdenstock, Brooklyn, N. Y., assignor to Chas. Pfizer & Co., Inc., New York, N. Y., a corporation of Delaware

No Drawing. Application September 15, 1949, Serial No. 115,957

2 Claims. (Cl. 226—89)

1

This invention relates to a rubber stopper having improved properties which is adapted for use in machines for automatically and mechanically stoppering vials or bottles. In particular, this invention relates to rubber stoppers having improved properties and which are adapted for use in packaging certain drugs and therapeutic materials in bottles or vials under sterile conditions.

In the past considerable difficulty has been encountered in the operation of automatic stoppering machines using sterile, dry stoppers. After sterilization, the stoppers tend to adhere to each other in masses preventing proper feeding, jamming the machines, and causing expensive delays in operation. Once the stoppers have passed from the feed hopper into that section of the machine leading to the mechanism which inserts them into the vials or bottles, they continue to cause difficulty. They do not roll or slide readily over the metal guiding surfaces, but rather tend to adhere to them instead of moving into the section of the machine which positions the stoppers just prior to insertion. Even momentary adherence to the metal surfaces causes difficulty. Thus, it can be seen that any method of preventing such adherence of stoppers both to one another and to the metal surfaces of machines in which they are utilized is of great importance, and constitutes a valuable contribution to the art.

Various methods have been resorted to in order to overcome these difficulties. Rubber stoppers have been washed, sterilized and dried in a variety of manners but with little improvement in the properties needed to provide a trouble-free operation in the automatic machines. Paraffin has been incorporated in rubber stoppers during their manufacture in such a manner that a surface coating slowly forms. This assists in making the stoppers free flowing, but there is a marked tendency for flakes of paraffin to become detached from the stoppers, particularly when a hypodermic needle is passed through the stopper in a vial in order to withdraw a solution therefrom. This is particularly undesirable when the solution is to be used for parenteral administration.

Lubrication of the metal surfaces of the machines over which the rubber stoppers must roll or slide with such materials as castor oil or mineral oil makes a temporary improvement in this operation, but it does not prevent the ad-

2

lubricated surfaces during continued operation of the machine soon removes the lubricants.

It has now been found that an improved rubber stopper which is suitable for use as a bottle or vial closure and which is admirably adapted for use in automatic stoppering machines without encountering the above-mentioned disadvantages can be prepared by coating the stopper with a thin film of a high boiling (that is, essentially non-volatile at normal temperature and atmospheric pressure) rubber lubricant, liquid at room temperature, which is stable to steam at 20 lbs. pressure for at least ½ hour and which has a viscosity of from 50 to 500 centistokes at room temperature. Rubber stoppers so coated can be sterilized and dried in the customary manner. The sterile stoppers may then be fed into the machine used in inserting the stoppers in vials or bottles. The stoppers do not adhere to one another, they do not obstruct the mechanism for feeding them from the hopper into the operating section of the machine. They do not adhere to the metal surfaces of the machine, but rather slide or roll readily into position where they are picked up and inserted in the mouth of the bottle or vial. No jamming of the machines by the stoppers involving costly delays is encountered. In addition to the above advantages the stoppers prepared by the disclosed process may be inserted into bottles and vials with much greater ease than is the case with untreated, sterilized and dried stoppers. The pressure required to insert the treated stoppers is less, and there is less tendency for them to pop out once inserted. This is true no matter what machine or method is used for placing the stoppers in the mouth of the bottle or vial.

Rubber stoppers which may be used in the process of this invention consist of natural rubber compounded in the usual manner, reclaimed rubber or synthetic rubber, e. g. neoprene. The treatment may be applied to rubber stoppers of various sizes, operating successfully with large or small stoppers. The lubricants which may be used in this invention include the silicone oils. The silicone oils are mixtures of methyl polysiloxanes of various molecular weights and vary in viscosity. I prefer to use a silicone oil having a viscosity of about 100 centistokes, but those of somewhat higher or lower viscosity, that is, from 50 to 500 centistokes are operable. In addition certain vegetable oils such as sesame or peanut oil which are stable to sterilization and

citrate and tributyl phthalate also possess suitable properties for use in this invention.

In a preferred method of applying the thin film of lubricant to the rubber stoppers for use in the automatic stoppering machine a silicone oil having a viscosity of from 50 to 500 centistokes is dissolved in a solvent, for example chloroform or carbon tetrachloride, and the stoppers are dipped in the lubricant and are drained, dried and sterilized. The concentration of silicone oil in the solvent may vary considerably. Thus, a solution of from 0.1% to 5% of silicone oil in a solvent may be used. It is preferred, however, to use a solution containing from 0.2 to 1.5% of silicone oil. Other lubricants in the same concentrations in suitable solvents can be similarly employed for coating the stoppers.

The manner of application of the selected lubricant can be varied considerably. The stoppers can be dipped directly in the lubricant and the excess removed. This method is not recommended, however, since it tends to leave excessive amounts of the liquid on the surface of the stopper. The lubricating liquid can also be applied to the stoppers by subjecting them to a fine spray of the liquid in a device suitable for agitating the stoppers so that they are coated evenly on all surfaces. The silicone oils may be applied in the form of an emulsion in water, such as "Silicone Emulsion 35A" (a stable emulsion of a silicone oil in water, manufactured by the Dow-Corning Corporation).

The selected lubricant can be applied batchwise as by agitation in a suitable vessel or it may be applied in a continuous manner, as by passage of the stoppers on a continuous conveyance through a zone in which the lubricant is applied in the form of the pure liquid, a solution, or a spray of either of these.

Rather than apply the silicone oils as such to the rubber stoppers, it is possible to form a suitable lubricating coating of a polymeric silicone on the surface of the rubber by exposing the latter to a precursor for the silicones. Thus, if rubber stoppers, bearing a thin film of water normally present on such surfaces, are exposed to the vapors of such a product as Dri-Film (a mixture of methylchlorosilanes manufactured by General Electric Corp.) for sufficient time a film of the silicone will be formed by reaction with water. Another material suitable for use in such treatment is dimethyl-dichlorosilane manufactured by the Dow-Corning Corporation.

The product of these various methods of treatment is a rubber stopper which may be sterilized with steam in the usual manner, dried and is then suitable for use in automatic bottle stoppering machines of various types. One such device is the automatic vial stoppering machine manufactured by the Afotex Products Company of New Brunswick, New Jersey.

The following example is given by way of illustration and is not intended to limit in any way the scope or spirit of the invention.

Example

A batch of approximately one hundred red, virgin rubber stoppers (standard size to fit 20 cc. penicillin bottles) was placed in a beaker and covered with a 1.5% solution of Dow-Corning Corporation 100 centistokes silicone oil in chloroform. After agitating the stoppers for a short time, the solution was removed from the beaker and the stoppers were allowed to drain. The coated stoppers were then placed in a covered metal tray in a clinical autoclave and sterilized for one-half hour at 20 pounds per square inch steam pressure. The tray was then placed in a dryer where they were subjected to a temperature of 108° F. for four hours. Inspection of the stoppers showed them to be perfectly free-flowing adhering neither to one another nor to any smooth, slanted surface. The stoppers were placed in the hopper of an automatic vial stoppering machine (that of the Afotex Products Company) and the machine was started. The stoppers fed faultlessly from the hopper into the slotted annular ring of the machine, down the grooved chute to the lower end where they were picked up by the vacuum operated head which inserted them in the glass bottles. There was no adhesion of the stoppers in the hopper; there was no adhesion to the metal walls of the hopper, to those of the annular ring or to those of the chute. The stoppers fed steadily and as rapidly as they were required to the point at which they were picked up for insertion. There was no jamming of the machine and no shut-downs as had been encountered with stoppers not treated by the process of this invention.

This invention is not restricted to natural, reclaimed or synthetic rubber stoppers, but may be applied to any type of bottle or vial closure which because of its composition and the manner in which it must be handled in automatic stoppering machines causes difficulty due to adhesion to one another or to parts of the machine.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that this invention is not limited to the specific embodiments hereof, except as defined in the appended claims.

I claim:

1. A rubber stopper suitable for use as a closure for pharmaceutical containers, and particularly adapted for use in conjunction with an automatic stoppering machine, which stopper is coated with a thin film of a silicone oil having a viscosity of from 50 to 500 centistokes at room temperature and is heat-sterilized.

2. A process for stoppering pharmaceutical containers which comprises coating rubber stoppers with a thin film of a silicone oil, sterilizing the coated stopper with steam at elevated pressure, drying the sterilized stoppers and inserting the same under aseptic conditions in the mouths of said pharmaceutical containers.

ROBERT R. UMBDENSTOCK.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
65,533	Bishop	June 11, 1867
726,629	Brown	Apr. 28, 1903
811,876	Schroeder	Feb. 6, 1906
2,386,466	Hyde	Oct. 9, 1945
2,442,059	Safford	May 25, 1948
2,470,772	Haas	May 24, 1949
2,471,224	Loughborough	May 24, 1949
2,474,704	Thayer	June 28, 1949
2,494,920	Warrick	Jan. 17, 1950
2,573,637	Bender	Oct. 30, 1951