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AND APPARATUS FOR MAKING SAME

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2 Sheets-Sheet 1

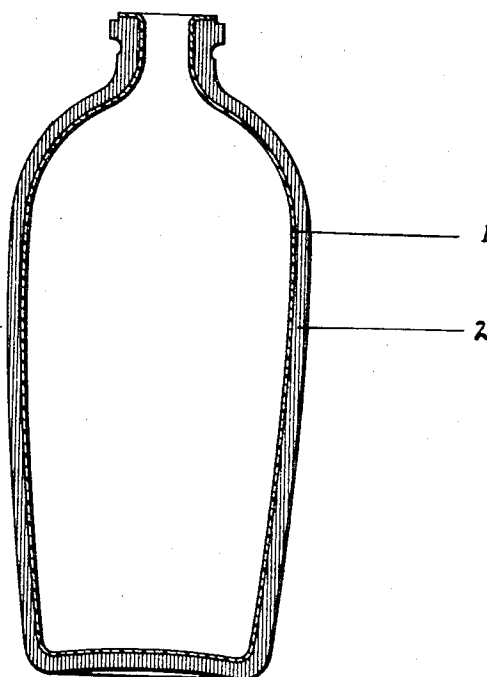


FIG. 1

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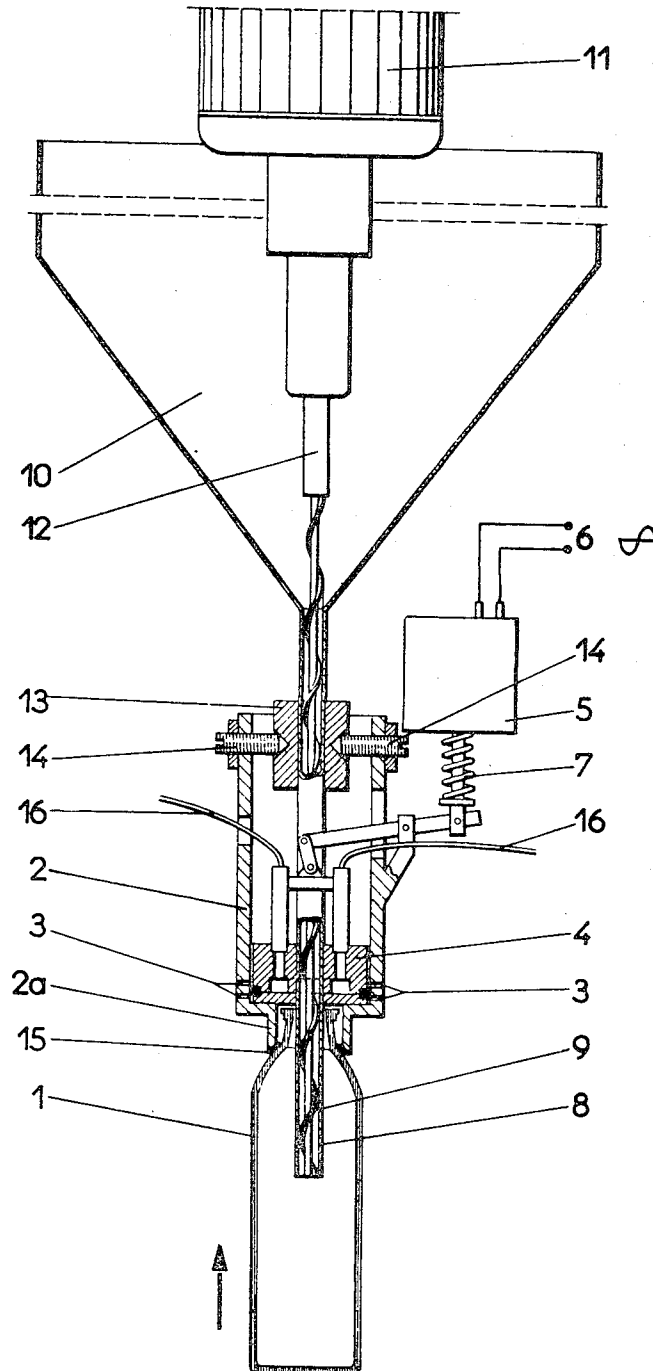


Fig. 2

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## GLASS CONTAINERS FOR AEROSOLS AND METHOD AND APPARATUS FOR MAKING SAME

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Continuation-in-part of applications Ser. No. 665,798, Sept. 16, 1967, now abandoned, and Ser. No. 843,617, July 22, 1969, now Patent No. 3,611,990. This application June 30, 1970, Ser. No. 51,229

Claims priority, application France, Sept. 9, 1966, 75,913

Int. Cl. B44d 1/94

U.S. Cl. 117—18

10 Claims

### ABSTRACT OF THE DISCLOSURE

A fluid containing a polymerizable film forming substance is introduced into a container so as to adhere to the inner walls thereof. The non-adhering portion of the liquid is then withdrawn and the remainder polymerized in situ on the inner surface of the container. Alternatively, the container is a mold coated with a parting compound and the film formed therein is separated from said mold after polymerization.

### SUMMARY OF THE INVENTION

This application is a continuation-in-part of our prior applications Ser. No. 665,798, filed Sept. 16, 1967 now abandoned, and 843,617, filed July 22, 1969, now Pat. No. 3,611,990, issued Mar. 24, 1971.

This invention relates to containers for aerosols, and particularly those comprising a glass envelope. It is known that an internal pressure exists inside an aerosol container and that this pressure varies according to the products contained and the effects desired during use. This pressure, usually supplied by a liquefied gas, is normally about 4 kg./cm.<sup>2</sup> at 20° C. When the temperature rises to 30° C., as usually happens when the container is tested for tightness in water baths at the factory or when the user leaves it on a shelf near a radiator for example, or at the store when it is displayed in a window in full sunlight, the pressure increases significantly and may reach 5 to 7 kg./cm.<sup>2</sup>. It is therefore necessary to have containers capable of withstanding an absolute internal pressure of 8 kg./cm.<sup>2</sup>.

But this is not enough. When a glass aerosol bottle breaks due to a defect, a blow, or a fall, it poses a great hazard unless the outward propulsion under pressure of the splinters can be avoided.

To remedy this, it is known that the glass may be made more resistant to shock by surface treatments of the titani- zation type, as in the so-called "hardcote" process; however, these treatments only change the limits of breaking due to shock without changing its effects.

The outward propulsion of splinters may also be lessened by wrapping the container in a plasticized and jellified polyvinyl chloride, for example the product called "plastisol." One or more judiciously placed vents permit, in principle, the escape of the product and the gas under pressure while preventing shattering of the glass.

Nevertheless, this technique is rather uncertain, since depending on the manner in which the shock and fragmentation of the splinter occurs, the bottle may be projected violently in any direction like a rocket by the gas escaping through the vents. If, on the other hand, a splinter of glass blocks the vent or vents, the plastic envelope swells as if made of gold-beater's skin and the valve is usually ejected because the envelope becomes separated from it. The glass splinters may also pierce or tear

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the plastic envelope and then be projected outward. Finally, even when the vents operate normally, the liquid contained in the bottle is spread all over the area of the fall, which can be bothersome if it is, for example, a dyeing agent.

The objects of the present invention are accordingly to eliminate these disadvantages by providing:

(1) A method of applying coatings or linings of plastic material to the inside of hollow containers of any shape or nature;

(2) The new article of manufacture which consists of a container produced by said processes;

(3) Apparatus adapted to carry out said process, using powdered materials.

A secondary feature of the invention is that it provides a process of producing hollow containers consisting entirely of a fused plastic film inside a heated mold which has been coated with a parting compound and from which said film may be removed.

The coating method in question may be carried out by utilizing various products in either liquid or powdered form.

In particular, it envisages the protection of glass containers which are to hold products under pressure such as containers for aerosol.

If the container breaks or explodes the plastic linings make it possible to prevent the outward projecting of fragments and the accidents which may result therefrom.

By way of example, to illustrate the present invention, the covering or lining applied to the inside of the bottle may be of a plastic material, rubber or any other unbreakable material which will not tear instantly due to a physical or thermal shock.

If the covering is formed from an originally liquid material the application may be made in the bottle:

By applying a liquid resin or "plastisol" by means of an air brush and subsequently polymerizing it by the application of heat or by adding a catalyst to produce cold polymerization;

By filling the bottle with a resin or "plastisol" and emptying out the excess, the layer sticking to the inside wall then being polymerized as described above;

By centrifuging the bottle into which has been introduced before or during the centrifuging, a liquid resin or "plastisol" which is then polymerized by the application of heat or by adding a catalyst to produce cold polymerization, during or after the centrifuging operation;

By centrifuging the heated bottle into which has been introduced a liquid resin or "plastisol" which is polymerized on contact with the hot glass.

If the covering consists of a flexible lining introduced into the bottle, it may be applied:

By introducing into the bottle a flexible lining which, upon blowing into the bottle or filling it with a liquid conforms to the shape of the bottle, the inside wall of which has previously been covered with an adhesive applied with an air brush or by filling and removal of the excess;

By introduction into the bottle of a flexible lining which is attached by means of an adhesive to the interior or exterior of the ring on which the valve is mounted and which is formed into shape by blowing into the bottle or by filling it with a liquid;

By introduction into the bottle of a flexible lining which, by blowing into the bottle, is formed into the shape of the hot bottle and becomes fastened to it;

By introduction into the bottle of a flexible partially polymerized lining which by blowing into the bottle, is formed into the shape of the hot bottle and completes its polymerization by contact with the hot glass.

The lining material may be introduced in either liquid or powdered form.

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In order to store aqueous products it is preferred to use plastisols or organosols consisting of dispersions of very fine resinous particles in solvents or plasticizers, or in mixtures of such solvents or plasticizers, possibly in association with colored pigments.

Vinyl plastisols and organosols are particularly useful. Depending on the nature of the coating product used, it is sometimes necessary to first apply an adhesive layer consisting, for example, of a product having an acrylic resin base to the inner wall of the container before applying the plastic coating itself.

In order to facilitate the application of such a dispersion, or such other dispersions as polyurethane, polyesters, and catalyzed epoxy products, which are more resistant to the action of solvents, essences and essential oils which do not swell, dissolve, or cause them to deteriorate, when the containers are designed to hold non-aqueous products, the container to be coated is first brought to a suitable temperature, which may for example be from 150–160° C. for a plastisol having a polyvinyl chloride base.

The container is then filled with the said liquid product, so as to entirely cover the inner wall of the container. This is done under a certain gaseous pressure which tends to apply the dispersion to the inner wall of the container.

At the end of from 15–40 seconds, for example, depending on how thick a dry film is desired, the excess liquid which has not adhered to the wall is withdrawn by means of a suction tube of any suitable shape.

The temperature of the container and the gel adhering to its inner wall is then increased, for example, to from 180°–200° C. for a time between 5 and 20 minutes so as to cause the polymerization of the internal coating, which then takes the form of a continuous flexible film of constant thickness.

Depending on whether a primary adhesive layer has been applied, or on the contrary an anti-adhesive layer, and particularly a coating of the phenolic epoxy type containing a parting compound such, for example, as the one sold in the United States under the trademark "Acrawax" by the Glyco Chemical Co. and sold in France by the Organon Company, the coating will adhere or fail to adhere to the internal wall of the container or of the heating mold.

The process according to the invention may also be carried out by using powdered polyolefines, polyamides, epoxy resins, or polyvinyl chloride powders.

These powders are first modified by adding anti-static compounds, dyes, stabilizers, and possibly pigments. The grade and granulometry of these powders are, in the case of a polyolefine, between 40 and 70 and between 100 and 300 microns respectively.

The homogeneous mixture prepared in this manner is injected into a container which has first been heated to a temperature of the order of 200°–250° C. This injection may be made by using a screw or a piston.

When the container is full of powder to the height to which it is to be coated, the system is hermetically sealed and the powder therein placed under a pressure of about 2 kg./cm.<sup>2</sup> for several seconds. The excess powder which does not adhere to the inner wall of the container is then removed, possibly after a certain lapse of time, by means of a vacuum pump or any other adequate apparatus.

The container and the mixture adhering to its inner wall are then heated to a temperature of the order of 230° C., for example, for several minutes, so as to fuse the coating until a continuous film is obtained. This coating is flexible and of constant thickness and is more or less adherent to the wall of the container.

The thickness of the flexible lining or covering may vary according to the use for which the glass aerosol is intended. The inside protective layer may be furnished with vents or not, as desired or needed. This protective layer may also reach to the upper edge of the neck of the bottle, pass over the horizontal part of this piece,

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project to the outside, or be formed in one piece with an external protecting layer, if there is one, particularly if the layer is applied by filling with a liquid and then emptying out the excess. If the covering extends to the upper part of the neck, it may replace the sealing ring of the valve cap.

In the case of a bottle the outside of which is covered with a plastic material, the use according to the invention of an internal covering removes the previously indicated danger of violent movements in all directions, since the internal covering retains the product under pressure or slows its escape if it is furnished with vents. It also avoids swelling of the envelope which may lead to the propulsion of glass splinters if the valve is ejected. Indeed, the liquid under pressure is retained by the internal lining and is ejected only if the valve is ejected. If the valve is not ejected, the internal lining retains the product under pressure and eliminates or greatly reduces the swelling.

The use of the invention also prevents the external covering from being violently torn when pieces of glass are propelled outward, since the internal lining retains the product under pressure. Finally the flow of the liquid is slowed by the internal lining and the risk of stains is lessened.

On the other hand, in the case in which the invention is applied to a bottle which does not have an outside plastic covering, the inside plastic layer, when thick enough, prevents on the one hand the violent movement in any direction of the glass bottle when it is dropped, as well as the propulsion of splinters, due to the fact that the wall of glass breaks normally and the internal lining then swells, or if pierced by a splinter of glass permits the liquid under pressure to escape while the already broken glass can no longer be projected. The plastic lining or covering thus deadens the shock and adsorbs most of the initial energy of the expansion of the gases.

On the other hand, frequently the plastic lining is not pierced by glass splinters, since they are outside it, so that the risk that the product will spread is lessened. The lining swells under the effect of the pressure while retaining the product it contains and it may be pierced and emptied somewhere where it will cause no damage. Only an unseating of the valve permits the product to be removed.

In any case, the aerosol bottle according to the invention is obviously safer to use.

Several representative examples of specific methods of carrying out the invention will now be given, followed by a description of suitable apparatus for use in connection therewith. This apparatus and its product are illustrated in the accompanying drawings, in which:

FIG. 1 is a vertical sectional view taken through a bottle according to the invention; and

FIG. 2 is a vertical view, partly in elevation and partly in section, showing said apparatus.

#### EXAMPLE 1

A colorless liquid product is used which has the following composition:

|                                                                                                                                        |                       |      |
|----------------------------------------------------------------------------------------------------------------------------------------|-----------------------|------|
| Polyvinyl chloride having a molecular weight between 80,000 and 140,000                                                                | --- percent by weight | 44.5 |
| Diethyl-2-hexylphthalate                                                                                                               | -----do-----          | 30   |
| Didecyl adipate                                                                                                                        | -----do-----          | 44.5 |
| Octyl epoxy stearate (manufactured by the Argus Co. in the United States and sold in France by the Sogefra Division of the S.C.E. Co.) | -----do-----          | 10   |
| Tri-(2-chloro-ethyl) phosphate                                                                                                         | -----do-----          | 7.8  |
| Stabilizer having a barium, cadmium and zinc base (sold under the trademark Mark K C B by the Sogefra Division of the S.C.E. Co.)      | --- percent---        | 1.3  |
| Optical azuring product                                                                                                                | -----do-----          | 0.3  |
| Fluidizer sold under the trademark Dehydrol by the German Henkel Co.                                                                   | -----do-----          | 1.1  |

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Such a product loses at most 0.5% by weight of water during the above coating process.

The density of the coating obtained falls between 1.15 and 1.20.

At the moment of its injection the liquid has a viscosity at a temperature of 20° C. which falls between 1500 and 2500 centipoises.

The container is preheated to a temperature between 150° and 160° C.

The plastisol is injected through a tube up to the desired level under a gaseous pressure between 7 and 8 kg./cm.<sup>2</sup>.

The plastisol is left in contact with the container for 20 to 30 seconds.

The excess plastisol is eliminated by means of a vacuum pump.

The container with its internal coating is then placed in an oven at a temperature between 175° and 180° C. for from 10 to 15 minutes.

The result is a coating 1a having a thickness between 0.5 and 1 millimeter.

It should be noted that the group of plasticizers mentioned above, which represent a total of 52.8% of the mixture, may represent any proportion between 70% and 40%. In like manner the quantity of polyvinyl chloride may vary from 30-60%, these different proportions being a function of the degree of flexibility and rigidity of the film which is desired and the resistance to cold which is to be obtained.

#### EXAMPLE 2

The procedure is exactly the same as in Example 1 except that a colored liquid product having the following proportions is used:

|                                                              |                        |      |
|--------------------------------------------------------------|------------------------|------|
| Polyvinyl chloride                                           | -----percent by weight | 45.5 |
| Various plastifiers of the four types mentioned in Example 1 | -----percent           | 49.1 |
| Stabilizer of the type given in Example 1                    | ---do---               | 1.2  |
| Fluidizer of the type given in Example 1                     | ---do---               | 1.1  |
| Pigments                                                     | -----do---             | 2.7  |

#### EXAMPLE 3

A powdered product having the following composition is used:

|                                                                                    |                      |      |
|------------------------------------------------------------------------------------|----------------------|------|
| 40 to 70 grade polyolefine having a granulometry between 100 and 300 microns       | ---percent by weight | 97.7 |
| Stearamidopropyl - dimethyl-hydroxyethyl-ammonium nitrate (as an antistatic agent) | -----percent         | 1.2  |
| Optical azuring product                                                            | -----do---           | 0.1  |
| 2,4 - di-hydroxybenzophorone (as a light stabilizer)                               | -----do---           | 0.3  |
| 4,4'-thio-bis-(3-methyl-6-tertiobutyl phenol) (as a heat stabilizer)               | -----do---           | 0.7  |

It should be noted that, instead of the above nitrate, it is possible to use a synthetic wax such as the one sold under the trademark "Articire" in France by the Lamotte and Coiffard Co., as an anti-static agent.

It should also be noted that no useful purpose is served by using higher percentages of the anti-static agent or thermal stabilizer.

The container itself is preheated to a temperature between 200-230° C. The pulverulent mixture is then injected by means of a screw or piston, while providing means for air to escape from the container.

When the container is full the system is hermetically closed and the screw is again actuated to produce a pressure of the order of 2 kg./cm.<sup>2</sup> in the container.

The powder is left in contact with the container for several seconds, for example 2-3 seconds. Then the excess mixture is eliminated by means of a vacuum pump or other suitable device.

The container, with its coating, is then placed in an oven at a temperature between 210-230° C. for 5-7 min-

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utes. The resulting lining has a thickness of 0.8-1.2 millimeters.

The loss of water during cooling should not exceed 0.5%; the apparent density of the powder used is 0.34; and the density of the film obtained is 0.92. The granulometry of the product used is between 100 and 300 microns, with a grade between 40 and 70.

The melting point of the powder and the film obtained is 109° C. The foregoing compositions may naturally be modified depending on the opacity, the flexibility, and the mechanical strength required.

#### EXAMPLE 4

The procedure is exactly the same as in Example 3 except that a mixture having the following composition is used:

|                                                               |         |     |
|---------------------------------------------------------------|---------|-----|
|                                                               | Percent |     |
| Polyolefine having the grade and granulometry specified above | -----   | 95  |
| Anti-static agent of the above mentioned nitrate type         | -----   | 1.1 |
| Optical azuring product                                       | -----   | 0.1 |
| Light stabilizer of the type specified                        | -----   | 0.3 |
| Heat stabilizer of one of the two types specified             | -----   | 0.7 |
| Pigments                                                      | -----   | 2.6 |

Of course, the quantity of pigments depends upon the color desired and may require the percentages of the other constituents to be slightly modified.

The process which has just been described may be applied to any type of container or can, made of glass, metal, or any other material.

Moreover, as has been indicated above, it is possible, by providing an anti-adhesive undercoating consisting of a glaze of the phenolic epoxy type containing a parting compound, such, for example, as Acrawax sold by the Glyco Chemical Co., in the United States and by the Organon Co., in France to utilize as containers heated molds from which the film may be removed.

It will be readily understood that in this case it is unnecessary to place the container in an oven. If the mold is electrically heated, for example, it suffices to increase the intensity of the heating current so as to bring the heating mold to the required temperature, for example 180° C., for from 10-15 minutes in the case of a plastisol having a polyvinyl chloride base or 210°-230° C. for 5-7 minutes in the case of a polyolefine coating.

Turning now to the apparatus used in carrying out the invention, FIG. 2 of the drawings shows a container 1 which is heated to the desired temperature. A cylinder 2, the lower part of which is provided with vents 3, makes it possible when the piston 4 is raised, that is to say when the electromagnet 5 is not supplied by the AC source 6, and the piston 4 is held up by the spring 7, to force out the air in the container 1, as the powder is introduced through the tube 8 containing an Archimedes screw 9, which serves to advance the powder contained in the funnel 10. A motor 11 drives a rod 12 fixed to the Archimedes screw 9, and the assembly comprising the funnel 10 and a tube 8 is centered by centering means 13 comprising screws 14.

When the container is completely filled with powder and the air has been permitted to escape through the vents 3, the electromagnet 5 is actuated in such a way as to force the piston toward the bottom of the cylinder 2, thus closing the vents 3, the container 1 being also forced against sealing means 15 carried by cylinder 2a of smaller diameter, located at the bottom of the cylinder 2.

When the piston 4 is in its lower position a pressure of the order of 2 kg. is applied to the powder by turning the screw 9 by means of a motor 11.

It will be appreciated that the embodiment of the injection means which has just been described may be modified or improved and that certain elements thereof

may be replaced by their mechanical equivalents without thereby departing from the basic principles of the invention.

In particular, it is possible, when manufacturing hollow containers consisting solely of a plastic film to prolong the duration of the injection of the liquid or powdered plastic so as to obtain a plastic film more than 1 millimeter thick.

Moreover, in this case, it is possible to use heating molds comprising several intercommunicating cells which are isolated one from the other, so as to produce at a single operation either several plastic containers or a multicellular container having plastic walls.

What is claimed is:

1. Method of forming a permanently adhering coating on the inner wall of a hollow container from a powdered coating material, which method comprises the steps of: first heating said container to a temperature sufficient to fuse said material, filling said container with said material at substantially atmospheric pressure while permitting air to escape from said container, pressurizing said container by applying a higher pressure to said material to force it against the inner surface of said container while preventing any further escape from said container, maintaining said material under said higher pressure until its outer layer fuses and adheres to said inner surface, removing any of said material which does not adhere to said container after a short lapse of time, and then heating said container to a temperature sufficient to fuse said coating material into a continuous film.
2. Process as claimed in claim 1 in which a first layer of adhesive material is applied to said inner wall before said coating material is injected into said container.
3. Method as claimed in claim 1 in which at least said higher pressure is mechanically applied.
4. Method as claimed in claim 1 in which said higher pressure is of the order of 2 kg./cm.<sup>2</sup>.
5. Method as claimed in claim 1 which comprises the

step of applying an anti-static agent with said coating material.

6. Method as claimed in claim 5 in which stearamido-propyl-dimethyl-hydroxyethyl ammonium nitrate is included in said coating material as an anti-static agent.

7. Process as claimed in claim 1 in which said coating product is selected from the group consisting of polyolefine, polyamide, epoxy resin and polyvinyl chloride powders.

8. Method as claimed in claim 7 in which said coating product is a polyolefine powder having a grade between 40 and 70 and a granulometry between 100 and 300 microns.

9. Process as claimed in claim 7 in which said powdered coating material is injected by means of an endless screw and which permits the air within said containers to be evacuated as they are being filled.

10. Container produced by the process of claim 1.

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117—21, 33, 97, 65.2, 47 H; 220—64; 264—302; 118—408