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MANUFACTURE OF ARTICLES FROM LIQUID DISPERSIONS

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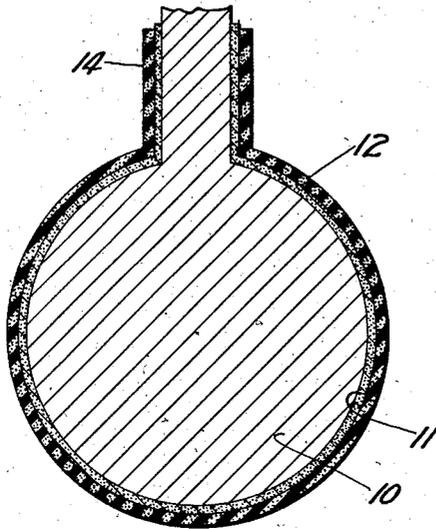


FIG. 1

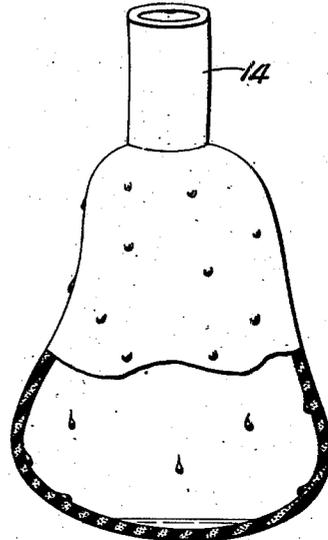


FIG. 2

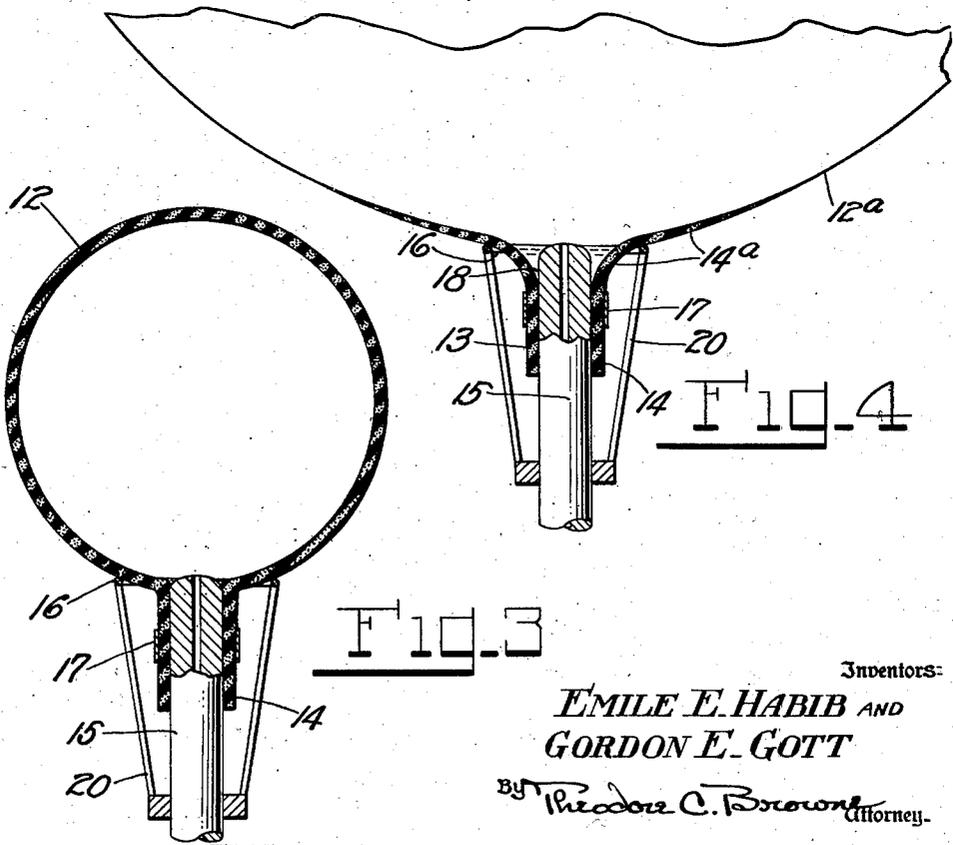


FIG. 3

FIG. 4

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## MANUFACTURE OF ARTICLES FROM LIQUID DISPERSIONS

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Application November 16, 1943, Serial No. 510,443

4 Claims. (Cl. 18—58)

The present invention relates to the manufacture of meteorological, radiosonde, and emergency life-saving balloons, and more particularly to an improvement in a dipping type process used in manufacturing these articles.

Balloons which are used to carry aloft weather recording instruments are quite large. The common sized balloon of this type is about three feet in diameter before ascension and expands during flight to 12 feet or more. Because of this requirement, such balloons had, until the recent past, been made by a casting procedure, as distinguished from a dipping procedure. In this casting process a sensitized latex dispersion is cast in a rotating, hollow, spherical mold immersed in a hot water bath. The process is slow and, especially when used with chloro butadiene-1,3, the preferred material for certain military balloons, is too sensitive to slight variations in time and temperature, and consequently requires too precise control for effective and economic factory use. This difficulty has, to a large extent, recently been overcome by introduction of a dipping type process, in which the formed deposit is stripped from the mold while it is still sufficiently soft from the presence of water to be capable of plastic (as distinguished from elastic) deformation, washed and then inflated while still plastic to permanently increase its size and make it more nearly spherical. This dipping process is described in detail in our co-pending application, Serial No. 510,442, filed on the same day as the present application. In practicing this process on a factory scale, it was found that a substantial percentage of the balloons burst during the inflation treatment before reaching the desired size. Investigation showed that the uninflated gel of specimens which burst was of uniform gauge over its entire area within extremely close tolerance limits, so close that the failures during inflation could not be accounted for on the basis of variations in wall thickness alone.

Further investigation led to the discovery that any droplets of water remaining on the surfaces of the plastic gel from the washing following dipping were immediately absorbed into the material during inflation. It was then discovered, from a study of the fragments of the burst specimens, that failure had occurred in those areas into which excess water had been absorbed. It is not possible to avoid wetting the gels, because they must be washed to remove the coagulant which remains on their inner surface. It is not possible to avoid local accumulations of water by drying the gels before inflation, because it is essential that the gels be still

plastic enough during inflation so that they can be sufficiently enlarged in size.

In accordance with the present invention, the percentage of failures in the manufacture of meteorological balloons by the coagulant dipping process referred to above is substantially reduced by removing any local accumulation of water from the surfaces of the plastic gel which is to be stretched during inflation before the inflation step is carried out. The invention will be more fully understood from a reference to the accompanying drawing, in which

Figure 1 is a sectional view of a dipping mold with the rubber deposit thereon;

Figure 2 is an elevation, partly broken away, of the stripped gel deposit;

Figure 3 shows in section the wet gel in position on the inflation nozzle; and

Figure 4 is similar to Figure 3, but shows a later stage in the inflation step.

In practicing the present invention, a coagulant bath and a dipping bath of compounded rubber dispersion are made up according to established practice in the dipping art. The following examples are illustrative of suitable coagulant and dipping compounds.

*Example 1.*—For a meteorological balloon made from a polymerized chloroprene-1,3 latex compound.

A dipping compound is made up in accordance with the following formula:

	Parts by weight of solids
35 Polymerized chloroprene-1,3 dispersion- (neoprene type 571) .....	100.00
Dibutyl sebacate emulsion .....	15.00
NH <sub>3</sub> (as ammonium hydroxide) .....	0.28
Hard clay (Suprex brand) .....	7.00
40 Dispersing agent (formaldehyde conden- sation product of naphthalene sul- phonic acid) .....	0.14
Zinc oxide (Kadox) .....	5.00
Phenyl beta naphthylamine .....	2.00
45 Casein solution (10%) .....	0.35
	129.77

The dibutyl sebacate emulsion has the following formula:

	Parts by weight
50 Dibutyl sebacate .....	35.00
Oleic acid .....	1.10
Wetting agent .....	0.10
Ammonium hydroxide (28%) .....	1.10
55 Water .....	13.05
	50.35

The formula for the casein solution is as follows:

	Parts by weight
Casein .....	3.50
Water .....	337.50
Ammonium hydroxide (28%) .....	7.50
	<hr/>
	348.50

The formula for the coagulant is as follows:

	Parts by weight
Bentonite .....	150
Water .....	900
Acetone .....	1,321
Calcium nitrate tetra hydrate .....	1,250
Glycerine .....	55
	<hr/>
	3,676

*Example 2.*—For a life-saving (captive) balloon to contain hydrogen:

	Parts by weight
Polymerized chloroprene-1,3 dispersion (neoprene type 571) .....	100.00
Ammonia (as ammonium hydroxide) .....	0.28
Hard clay (Suprex brand) .....	7.00
Dispersing agent (formaldehyde condensation product of naphthalene sulphonic acid) .....	0.14
Zinc oxide (Kadox) .....	5.00
Phenyl beta naphthylamine .....	2.00
Casein solution (10%) .....	0.35
	<hr/>
	114.77

The casein solution and coagulant have the composition described in Example 1.

*Example 3.*—For a balloon made from natural rubber latex; the dipping compound has the following composition:

	Parts by weight of solids
Rubber latex (60% solids) .....	100.00
Potassium hydroxide <sup>1</sup> .....	1.75
Zinc stearate .....	1.00
Zinc dibutyl dithiocarbamate .....	1.00
Symmetrical di-beta-naphthyl para phenylene diamine .....	1.00
Formaldehyde condensation product of naphthalene sulphonic acid .....	0.24
Titanium dioxide .....	1.00
Sulphur .....	1.10
	<hr/>
	107.09

<sup>1</sup> The amount will vary with different latices. Sufficient should be used to give the dispersion a viscosity suitable for dipping.

The coagulant has the following composition:

	Parts by weight
Bentonite .....	150
Water .....	900
Acetone .....	1,321
Calcium nitrate tetra hydrate .....	1,250
Glycerine .....	55
Glacial acetic acid .....	37
	<hr/>
	3,713

The ingredients are added in the order stated. In manufacturing balloons by the preferred form of the present process, a conventional balloon mold 10 is dipped in the coagulant to form a coating 11 of coagulant on its surface. The coated mold is then dipped in the bath of rubber dispersion, allowed to dwell therein for the time necessary to build up a rubber gel deposit 12 of the desired thickness, and then withdrawn

and held for a short time in still air at room temperature to permit coagulant to diffuse throughout the deposited layer 12 and complete coagulation of the very thin layer of uncoagulated dispersion which adheres to the outer surface of the coagulated gel 12 as it is withdrawn from the dipping bath. Before the gel has dried to any appreciable extent, it is stripped from the mold, inverted, and its neck portion 14 pulled over an inflation nozzle 15, arranged in a vertical position and having its orifice facing upwardly. A support for the soft gel is provided adjacent the inflation nozzle. As shown in Figure 3, the support takes the form of a ring 16 surrounding the nozzle orifice and supported by arms 20 mounted at their lower ends on the nozzle. Any excess liquid on the outside surface of the balloon will flow downwardly onto the neck, and most of it will drain away off the end of the neck. Excess water on the inside surface will likewise drain downwardly and collect at 18 in the neck area adjacent the nozzle. Air under a low pressure is then discharged through the nozzle into the gel, causing it to expand. As it expands, the rubber material undergoes plastic flow and the wall is permanently thinned; that is, upon release of pressure, the balloon does not contract to its original size as would an ordinary toy balloon.

When the gel has been fully expanded, it is dried in the expanded condition which permanently increases its size. The envelopes are then deflated and may be subsequently vulcanized, if desired, in air at 212° F.

The excess water on the inside surface of the balloon which collects during inflation at the bottom will be in contact with the gel only at its neck. The neck is stretched much less severely during the inflation than is the body portion; consequently excess water at this point does no harm.

The inflation nozzle may be arranged, if desired, to permit the excess water which drains from the inside surface of the balloon to flow out the nozzle. For example, a trap may be provided in the air line just below the nozzle.

The invention may be practiced also by swabbing or wiping the excess water from the surface of the gel before it is inflated, although we have found this procedure to be less convenient than the method described above. The swabs or cloths used for wiping should preferably be dusted with talc to prevent scuffing the gel.

It will be appreciated by those skilled in the art that the present invention is applicable to the manufacture of other dipped goods than meteorological and similar balloons. The process is applicable to the manufacture of any object which lends itself to manufacture by the coagulant dipping process of our application Serial No. 510,442, referred to above.

While the herein described process is particularly applicable to the polymerized halogen butadiene-1,3 and natural rubber illustrated in the examples, we believe it to be applicable to other elastomeric materials capable of being made in dispersion form from which coherent plastic gels can be coagulated. Accordingly, in the foregoing specification and in the claims we have used the word "rubber" in an inclusive sense.

We claim:

1. The method of making a hollow rubber object having an opening which comprises dipping a coagulant-coated mold of smaller size than the object into a liquid dispersion of rubber, with-

drawing the mold from the dispersion with a layer of rubber gel thereon, stripping the gel from the mold while the gel is still plastic from the presence of water, removing free water from the surface of the gel and enlarging the plastic gel to the desired size by inflating it, while it is still plastic from the presence of water interstitially present in the gel, and thereafter drying the gel.

2. The method of making a hollow rubber object having an opening which comprises dipping a coagulant-coated mold of smaller size than the object into a liquid dispersion of natural rubber, withdrawing the mold from the dispersion with a layer of natural rubber gel thereon, stripping the gel from the mold while the gel is still plastic from the presence of water, removing free water from the surface of the gel, and enlarging the plastic gel to the desired size by inflating it while it is still plastic from the presence of water interstitially present in the gel, and thereafter drying the gel.

3. The method of making a hollow rubber object having an opening which comprises dipping a coagulant-coated mold of smaller size than the object into a liquid dispersion of polymerized chloro butadiene-1,3, withdrawing the mold from

the dispersion with a layer of polymerized chloro butadiene-1,3 thereon, stripping the gel from the mold while the gel is still plastic from the presence of water, removing free water from the surface of the gel, and enlarging the plastic gel to the desired size by inflating it while it is still plastic from the presence of water interstitially present in the gel, and thereafter drying the gel.

4. The method of making a hollow rubber object having an opening which comprises dipping a coagulant-coated mold of smaller size than the desired size of the finished object into a liquid dispersion of rubber to deposit a layer of rubber gel thereon, withdrawing the mold from the dispersion with the layer of gel thereon, stripping the gel from the mold while the gel is still plastic from the presence of water, and removing free water from the surface of the gel and enlarging the gel to the desired size by inflating it in inverted position with its opening downward while it is still plastic from the presence of water interstitially present in the gel, and thereafter drying the gel.

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