United States Patent Office

3,245,566

Patented Apr. 12, 1966

3,245,566

CLOSURE CAP WITH PHENOLIC RESIN AND BUTADIENE-ACRYLONITRILE COPOLYMER MODIFIED VINYL PLASTISOL RESIN GASKET

Paul J. Szalay, Toledo, Ohio, assignor to Owens-Illinois Glass Company, a corporation of Ohio

No Drawing. Filed May 17, 1963, Ser. No. 281,363

13 Claims. (Cl. 215—40)

The present invention relates to improved plastisol gasket compositions and closures containing gaskets made from such compositions. More particularly, the invention relates to flow-in vinyl chloride plastisol gaskets as sealing means for container closures.

Many items today which are packaged in containers are susceptible to deterioration in quality unless packaged in hermetically sealed containers. This method of packaging is particularly important with respect to food products where it is desirable to employ a closure cap which will form a hermetic seal when the goods are initially sealed and is capable of being reapplied to form a hermetic seal to protect the unused portion of the contents.

Various types of closure caps have been employed in the past for providing hermetically sealed containers. Much of the work in this area has gone into improving the ability to apply and form a seal that will cooperate with the rim of the container and prevent the entrance of air into the container, so as to permit maximum storage time or shelf life for the contents of the container without spoilage.

One method for hermetically sealing containers which has become widely employed is the use of so-called "flow-in" type gaskets which are formed by flowing a material with a paste-like consistency into the closure and baking the gasket to make it firm. These flowable materials contain synthetic resins, plasticizers, fillers and the like and are known as "plastisols" in the art. Plastisol gaskets have been employed with a wide variety of closures, including rotatable closure caps for use particularly with glass containers.

In most cases the rotatable closure cap consists of a metal shell with a top panel portion and a depending skirt portion. The plastisol gasket composition is "flowed in" around the outer edge of the inner surface of the top panel portion, and may extend down the depending skirt portion. The top rim or edge of the container is pressed into this plastisol gasket when the cap is forced down into sealed relation with the container. The closure cap is provided with inwardly directed lugs attached to the depending skirt portion, whence comes the name "lug type" closure. The lugs on the closure are slidingly moved along threads or lugs formed in the outer rim along the top edge of the container. To seal the container, the closure cap is rotatably advanced onto the container, bringing the gasket into contact with the upper rim of the container. In many canning operations, the containers together with the contents are subjected to elevated temperatures for a period of time, so that the cap and the gasket therein must withstand such temperatures.

The plastisol gasket materials which have been employed in the past are dispersions of vinyl resins in nonvolatile plasticizers which have the consistency of a paste. At higher temperatures the paste becomes gel-like and loses its fluidity. The change in physical properties is brought about by solution of the resin in the plasticizer as the temperature is increased. At about 175° C. fusion takes place, resulting in a tough, rubbery mass.

Although these plastisol gaskets have been extensively used, a number of drawbacks have been associated there-

shelf life of packaged goods and, moreover, results in a closure cap which will not form a hermetic seal when reapplied to protect the unused portion of the container contents.

A further drawback of the known plastisol gasket compositions is their poor impact resistance. When containers fitted with closure caps containing plastisol gaskets are packaged or handled in distribution from the manufacturer to the final consumer, the containers are often jarred or bumped against each other or against the caps of adjoining containers. These impacts cause certain changes in the dimensions of the plastisol gasket and, if the gasket material has poor resiliency, it will fail to return to its original dimensions and hence leakage results from the failure of the gasket material. Similarly, the impact may cause a break or crevice between the gasket and the closure cap, permitting air to leak into the container thus impairing the seal and spoiling the product. The leakages will produce not only contamination of the product but loss of material as well.

A further characteristic of many of the plastisol gasket compositions of the past has been their susceptibility to seizing up in place, often making it necessary for the consumer to apply excessive torque to remove the cap. This phenomenon is physical in nature and occurs because of the poor aging characteristics of vinyl plastisols. The friction between the plastisol gasket and the container increases rapidly with standing. While the torque required to open the container immediately after sealing may be low, namely, in the range of from 5 to 25 inch pounds, it may increase after one day to 35 to 50 inch pounds. The ideal range for torque removal has been found to be from about 15 to 25 inch pounds regardless of the interval of time between initial capping and removal.

It is, accordingly, the object of this invention to avoid the shortcomings and disadvantages of the prior-known plastisol gasket materials for closure caps.

It is a further object of this invention to provide a novel plastisol gasket for closure caps.

It is a further object of the present invention to provide plastisol gaskets for closure caps which have improved resiliency and impact resistance, thus assuring a hermetic seal between the cap and the container.

It is a still further object of the present invention to provide a sealing gasket which permits low removal torque of the closure cap particularly when the contents of the container are sealed under vacuum.

In attaining the above objects, one feature of the present invention resides in the incorporation of particular ingredients in a plastisol composition to produce improved resiliency and impact resistance of a gasket formed therefrom.

A further feature of the present invention resides in the plastisol composition containing a liquid copolymer and a phenolic resin to improve the resiliency and impact resistance of the gasket formed therefrom.

These and other objects and features will become apparent to those skilled in the art from the following detailed description of the present invention.

It has now been discovered that a plastisol gasket composition of the "flow-in" type can be produced possessing good resiliency and impact resistance characteristics by the incorporation therein of particular polymers. The resulting closure caps containing the plastisol gasket of this invention can be removed from the container with a relatively low removal torque regardless of the lapse of time after the initial capping operation.

It has been found that by incorporating a liquid composition, the resulting plastisol gasket will be characterized by improved resiliency and impact resistance.

The plastisol composition which is employed for the purposes of the present invention is in the form of a paste-forming resin-plasticizer mixture containing a finely divided synthetic resin suspended in non-volatile plasticizers for the resin, the resin being paste-forming with the plasticizers at a temperature below the fluxing temperature of the resin plasticizer component and soluble in the plasticizer upon heating to the fluxing temperature. The plastisol composition may further contain finely divided filler and pigment material as well as stabilizers in a uniform distribution.

The liquid butadiene-acrylonitrile copolymer contains from about 20% to about 40% by weight of acrylonitrile in polymerized form.

A particularly useful liquid copolymer for the purpose of this invention contains about 37% by weight acrylonitrile in polymerized form. While the amount of liquid copolymer employed will be that which is sufficient to impart the desired properties to the plastisol gasket, use of about 1% to about 5% by weight based on the weight of the vinyl resin, is suitable, and use of about 3% to about 4% by weight gives excellent results

The phenolic resinoid component of the plastisol composition is a two-step novolak resin. The novolaks are produced from the reaction of less than equivalent amounts of formaldehyde with phenol, about 1:08 mole ratio although this can be varied in an acid catalyzed reaction. Novolak resins with an average molecular weight of up to about 1200 can be used although those resins in the medium molecular weight range, e.g. 650 amu, have been found to be particularly useful for this purpose. An example of the two-step phenolic novolak used for this purpose is that which is sold under the designation BRP 5012 by Union Carbide Corp. The phenolic novolak will be completely cured during the baking cycle for the gasket. The amount of phenolic novolak resin employed will be that which is sufficient to impart the desired properties to the plastisol gasket. Use of about 1% to about 5% by weight, based on the weight of the vinyl resin, has been found to give satisfactory results, while amounts of about 2% to about 4% are generally preferred.

Excellent properties are obtained by incorporating the above two polymers into the plastisol whereby the gasket materials produced from the plastisol compositions are able to withstand impact and possess improved recovery properties to prevent leakage and contamination of the contents of the container.

In forming the plastisol gasket composition, any of the numerous, commercially available vinyl chloride resins may be employed, preferably polyvinyl chloride of a high molecular weight in the range of about 60,000 to about 90,000, although higher molecular weights can also be employed. The polyvinyl chloride resin can be mixed with other vinyl polymers and copolymers. Copolymers of vinyl chloride with a minor amount of copolymerizable ethylenically unsaturated monomer can also be employed. Generally, a high percentage of the vinyl chloride must be present to obtain the high impact resistance, e.g., at least about 80% vinyl chloride. Included in the group of suitable comonomers are vinyl acetate, vinylidene, chloride, dialkyl maleates, maleic anhydride, and the like. It is understood that mixtures of comonomers can be employed provided the vinyl chloride is present in the amount of at least 80%.

The vinyl resin is uniformly distributed in and forms a paste with a plasticizer in which the resin is essentially insoluble at room temperature. At elevated temperatures, the resin is more soluble and dissolves in the hot plasticizer, resulting in a tough, rubbery mass.

An suitable plasticizer may be utilized as long as it is non-volatile and, when used for containers of food products, is non-toxic. Plasticizers such as polymeric

have been found suitable, although other conventional plasticizers can be used for this purpose. Included are dioctyl phthalate and other dialkyl esters of dicarboxylic acid, such as butyl decyl phthalate, octyl decyl phthalate, dioctyl sebacate, dibutyl sebacate, dioctyl adipate, dioctyl azelate, diisobutyl adipate, and other plasticizers such as butyl benzyl phthalate, tricresyl phosphate, polyethylene glycol adipate, alkyl esters of higher fatty acids and mixtures of two or more plasticizers, or one or more primary plasticizers with one or more secondary plasticizers. A plastisol composition which contains a polymeric ester-epoxide plasticizer of a relatively high molecular weight is preferred since this contributes good stability and good oil, water, and heat resistance to the gasket which is formed. The dibutyl sebacate is preferred as the dialkyl carboxylic acid ester plasticizer because it is completely odorless, non-toxic, and has good plasticizing effect on polyvinyl chloride in that it produces low temperature flexibility. Ordinarily, the total amount of plasticizer employed is not critical provided a sufficient amount is used to form a plastisol of suitable viscosity. Amounts varying from about 30% to 150% by weight based on the weight of vinyl resin are satisfactory, while amounts of about 50% to 90% are preferred.

It is also desirable to employ a filler material in the form of finely divided discrete particles which are uniformly distributed throughout the plastisol composition. The preferred filler material is titanium dioxide which functions both as a pigment and as a lubricant. However, other filler materials such as barytes, talc, calcium carbonate, clay such as bentonite, calcium silicate, carbon, finely divided silica, and diatomaceous earth may also be utilized. Other pigments can also be added if desired to impart any desired color, and for opaqueness. Up to about 20% or more filler may be added, although as little as about 0.5% based on the weight of vinyl chloride resin is preferably employed.

It is customary to employ a stabilizer for the plastisol gasket composition, and preferably one that is non-toxic if the gasket and closure are to be used for food containers. Calcium-zinc stabilizers, such as that sold commercially as Mark 34 by Argus Chemical Corporation of Brooklyn, N.Y., and Synpron 216 sold by Synthetic Products Co. of Cleveland, Ohio, have been found to yield good results. These are calcium-zinc soaps of higher fatty acids in the stearic range; that is, acids having from 16 to 22 carbon atoms. However, other materials functioning as stabilizers for vinyl chloride resin can also be used. Included are materials such as thio-organic tin compounds, metallic soaps, such as calcium, aluminum and zinc stearates, calcium laurate, barium laurate, magnesium stearate, alkyl and aryl tin compounds, dibutyl tin oxide, trioctyl phosphite, and the like. When used with processed food containers, it is important to employ a non-toxic material. Sufficient amounts of stabilizer are used to achieve the desired stabilizing effect, from about 0.4% to 1% based on the weight of the vinyl resin is usually adequate.

The viscosity and flow characteristics of the composition of the present invention may be modified by adding thereto a thinning agent such as an aliphatic or an aliphatic-aromatic hydrocarbon including mineral spirits, cyclohexane, and other petroleum distillates.

The plastisol gasket composition of this invention is made by blending the ingredients together in the usual mixing devices used for this purpose, for a sufficient time to produce the uniform, stable plastisol composition containing the liquid butadiene acrylonitrile copolymer and the phenolic novolak.

When used for processed food closure caps, the plastisol gasket must possess processing temperature resistance, be odor-free, non-toxic, and must not impart any flavor to the contents. The gasket composition of the present invention and impact resistance, and is further characterized by low removal torque.

An additional advantage of the plastisol gasket compositions of the present invention resides in the fact that complex milling procedures are not required. In carrying out the mixing operation, it is preferred to blend the ingredients briefly in a mixer such as a Hobart planetary action mixer. From ⅔ to ¾ of the mixed wet ingredients are added to the blend and mixing is continued for a few minutes at low speed. The mixing is increased to medium speed for 5 minutes, and to high speed for 10 minutes. The remaining wet ingredients are added to the mixture, and the ingredients are mixed for 5 minutes at high speed. Mixing is completed at low speed for about 10 minutes, and this sufficiently relieves the mixture of entrained air. If necessary, the mixing bowl may be cooled and the mixing times can be varied. Generally, 30 minutes of mixing is sufficient to insure a uniform product. It is preferable that the temperature of the mixing does not rise above about 35° C.

The following examples will serve to illustrate the present invention, but are not to be construed as limiting the scope of the invention in any manner.

EXAMPLE I

A plastisol composition was prepared containing the following ingredients in parts by weight:

Parts high molecular weight polyvinyl chloride (QYKV–2)	100
Parts phenol-formaldehyde novolak with a molecular weight of about 650 amu (BRP 5012)	2
Parts butadiene-acrylonitrile liquid copolymer containing about 37% by weight of acrylonitrile in polymerized form (Hycar 1312)	4
Parts polyester-epoxide plasticizer (Paraplex G–62)	50
Parts dibutyl sebacate plasticizer (Monoplex DBS)	4
Part titanium dioxide	1
Part calcium-zinc stabilizer (Synpron 216)	0.5

The ingredients above were blended for 30 minutes using a Hobart mixer at room temperature. The resulting paste was applied to conventional lug-type closure caps to form "flow-in" gaskets which exhibited improved recovery, tensile strength and impact resistance as shown in Tables I and II, infra.

EXAMPLE II

A plastisol gasket composition was made containing the following ingredients in parts by weight:

Parts high molecular weight polyvinyl chloride (QYKV–2)	100
Parts phenol-formaldehyde novolak with a molecular weight of about 650 amu (BRP 5012)	4
Parts butadiene-acrylonitrile liquid copolymer containing about 37% acrylonitrile in polymerized form (Hycar 1312)	5
Parts polyester-epoxide plasticizer (Paraplex G–62)	20
Parts dibutyl sebacate	34
Part titanium dioxide	1
Part calcium-zinc stabilizer	0.8

The ingredients were blended in a Hobart mixer for approximately 30 minutes. Thereafter the resulting paste was applied to conventional lug-type closure caps by the "flow-in" method. The caps showed good properties of impact resistance and improved removal torque.

EXAMPLE III

For purposes of comparison, two plastisol compositions identified as A and B were compounded and were identical with that of Example I with the exception that composition B contained no liquid butadiene-acrylonitrile copolymer. The compositions contained the following ingredients in parts by weight:

	Example I	A	B
Polyvinyl chloride	100	100	100
Phenolic novolak	2		2
Liquid butadiene-acrylonitrile copolymer	4	4	
Polymer ester epoxide plasticizer	50	50	50
Dibutyl sebacate	4	4	4
Titanium dioxide	1	1	1
Calcium-zinc stabilizer	0.5	0.5	0.5

The compositions of A and B were applied to the same conventional lug-type closure cap as employed in Example I. Physical test data were taken measuring the tensile strength of the plastisol gasket and the percent recovery after being subjected to a deformation. The deformation was carried out by compressing the gasket to 50% of its total original thickness employing a hard, round object for this purpose. The deformation was applied for one minute after which the gasket was released. The gaskets expanded to recover a portion of their original dimensions and the thickness was measured at the point where the deformation was applied. The values in Table I represent the percent of the thickness recovered after release. The percent recovery is thus an indication of the resiliency of the gasket material. The results are tabulated below and demonstrate that the gaskets of this invention have improved tensile strength and resiliency.

Table I

	Example I	A	B
Tensile strength in p.s.i.	1,940	828	1,740
Recovery percent after 1 minute of deformation	47.4	42.1	38.5

Further tests were carried out in order to assess the impact resistance of closure caps containing gaskets produced from the plastisol compositions of the present invention as compared with plastisol gasket materials representative of those which are commercially available identified as Plastisol Gasket A, Table II, infra. Impact resistance of the two groups of closure caps and gaskets was measured by filling the containers with water and placing the caps thereon with the contents being under vacuum. The containers were kept upside down and the cap closures subjected to an impact on the shoulder portion of the cap, i.e., between the top panel and depending skirt portion of the cap. The impact was provided by an impact tester comprising a rod with a small weight at one end and positioned to pivot in an arc about a point so that the weight struck the shoulder of the cap. Each cap was struck by the weight once on the shoulder portion adjacent each of its four lug positions, and then struck once on the shoulder portion in the area between two lug positions. After each blow, the water in the container was observed for bubble formation. If a single bubble was observed, it indicated that the seal was momentarily broken and then sealed again. Such a gasket is still deemed to provide a satisfactory seal. If a continuous stream of bubbles was formed, the gasket had failed to maintain a good seal and had exposed the contents to the atmosphere.

For purposes of measuring impact resistance, the arm of the impact tester was started at an arc of 65° and if no failure occured after the eight blows on the shoulder at the above-described positions, the arc was increased to 75°, then 85°, and up to 90°, on each container, until leakage and failure occurred. The results are set forth in Table II, with 8 closure caps and gaskets

Table II

Gaskets	Number of failures at—			
	65°	75°	85°	90°
Example I	0	0	0	0
Polyvinyl Chloride Plastisol Gasket	0	8	------	------

It will be noted that the gaskets of the present invention did not leak after an impact of 90°, while those which represent the conventional commercial gasket failed at an impact of only 75°, as measured by the impact tester.

Thus, the data demonstrates that closure caps provided with the plastisol gasket of the present invention is able to withstand substantially increased impacts without the seal being deleteriously affected.

It is understood that various other modifications will be apparent to and can readily be made by those skilled in the art without departing from the scope and spirit of this invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the description set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

What is claimed is:

1. In a closure cap in sealed relation with a container and having a vinyl chloride plastisol gasket disposed therein, and where said gasket has poor impact resistance and resiliency causing leakages and loss of vacuum in the container when the closure cap is subject to impact, the improvement in accordance with which the leakages and loss of vacuum are substantially eliminated when the closure cap is subjected to impact and which comprises having from about 1 to 5 parts by weight of a liquid butadiene-acrylonitrile copolymer and about 1 to 5 parts by weight of a phenol-formaldehyde novolak copolymer present in said vinyl chloride plastisol gasket, said copolymers being present together in an amount sufficient to improve the impact resistance and resiliency of said gasket, said parts by weight being based on 100 parts by weight of vinyl chloride resin in said plastisol.

2. In a closure cap in sealed relation with a container and having a vinyl chloride plastisol gasket disposed therein, and where said gasket has poor impact resistance and resiliency causing leakages and loss of vacuum in the container when the closure cap is subjected to impact, the improvement in accordance with which the leakages and loss of vacuum are substantially eliminated when the closure cap is subjected to impact and which comprises having from about 1 to 5 parts by weight of a liquid butadiene-acrylonitrile copolymer containing from about 20% to about 40% by weight of acrylonitrile in copolymerized form and about 1 to 5 parts by weight of a phenol-formaldehyde novolak copolymer present in said vinyl chloride plastisol gasket, said parts by weight being based on 100 parts by weight of vinyl chloride resin in said plastisol.

3. In a closure cap in sealed relation with a container and having a vinyl chloride plastisol gasket disposed therein, and where said gasket has poor impact resistance and resiliency causing leakages and loss of vacuum in the container when the closure cap is subjected to impact, the improvement in accordance with which the leakages and loss of vacuum are substantially eliminated when the closure cap is subjected to impact and which comprises having about 3 to 4 parts by weight of a liquid butadiene-acrylonitrile copolymer containing from about 20% to about 40% by weight of acrylonitrile in copolymerized form and about 2 to 4 parts by weight of a

vinyl chloride plastisol gasket, said parts by weight being based on 100 parts by weight of vinyl chloride resin in said plastisol.

4. In a closure cap in sealed relation with a container and having a vinyl chloride plastisol gasket disposed therein, and where said gasket has poor impact resistance and resiliency causing leakages and loss of vacuum in the container when the closure cap is subjected to impact, the improvement in accordance with which leakages and loss of vacuum are substantially eliminated when the closure cap is subjected to impact and which comprises having about 4 parts by weight of a liquid butadiene-acrylonitrile copolymer containing from about 20% to about 40% by weight of acrylonitrile in copolymerized form and about 2 parts by weight of a phenol-formaldehyde novolak copolymer present in said vinyl chloride plastisol gasket, said parts by weight being based on 100 parts by weight of vinyl chloride resin in said plastisol.

5. In a closure cap having a vinyl chloride plastisol gasket disposed therein and wherein said gasket has poor impact resistance and resiliency causing a deterioration of the seal when said closure cap is in sealed relation with a container and subjected to impact, the improvement whereby the impact resistance and resiliency are improved and which comprises having from about 1 to 5 parts by weight of a liquid butadiene-acrylonitrile copolymer containing about 20% to about 40% acrylonitrile by weight in polymerized form and about 1 to 5 parts by weight of a phenol-formaldehyde novolak copolymer present in said vinyl chloride plastisol gasket, said copolymers being present together in an amount sufficient to improve the impact resistance and resiliency of said gasket, said parts by weight being based on 100 parts by weight of vinyl chloride resin in said plastisol.

6. The closure cap as defined in claim **5** wherein said liquid butadiene-acrylonitrile copolymer is present in an amount to about 3 to 4 parts by weight of said vinyl chloride resin in said gasket.

7. A closure cap having a vinyl chloride plastisol gasket disposed therein, said gasket having a composition comprising a vinyl chloride dispersion resin and from about 1 to 5 parts by weight of a liquid butadiene-acrylonitrile copolymer and from about 1 to 5 parts by weight of a phenol-formaldehyde novolak copolymer in said plastisol, said parts by weight being based on 100 parts by weight of vinyl chloride resin in said plastisol.

8. A closure cap having a vinyl chloride plastisol gasket disposed therein, said gasket having a composition comprising a polyvinyl chloride dispersion resin and about 1 to 5 parts by weight of a liquid butadiene-acrylonitrile copolymer containing from about 20% to about 40% by weight of acrylonitrile in polymerized form and about 1 to 5 parts by weight of a phenol-formaldehyde novolak copolymer in said plastisol, said parts by weight being based on 100 parts by weight of vinyl chloride resin in said plastisol.

9. A closure cap having a vinyl chloride plastisol gasket disposed therein, said gasket having a composition comprising a polyvinyl chloride dispersion resin and from about 3 to 4 parts by weight of a liquid butadiene-acrylonitrile copolymer containing from about 20% to about 40% by weight of acrylonitrile in polymerized form and 2 to 4 parts by weight of a phenol-formaldehyde novolak copolymer in said plastisol, said parts by weight being based on 100 parts by weight of vinyl chloride resin in said plastisol.

10. A closure cap having a vinyl chloride plastisol gasket disposed therein, said gasket having a composition comprising 100 parts by weight polyvinyl chloride dispersion resin, from about 1 to 5 parts by weight of a liquid butadiene-acrylonitrile copolymer containing from about 20% to about 40% by weight of acrylonitrile in polymerized form, about 1 to 5 parts by weight of a phenol-

90 parts by weight of a plasticizer for said polyvinyl chloride.

11. A closure cap having a vinyl chloride plastisol gasket disposed therein, said gasket having a composition in parts by weight comprising

Vinyl chloride dispersion resin	100
Liquid butadiene-acrylonitrile copolymer	1–5
Phenol-formaldehyde copolymer (novolak)	1–5
Polymeric ester epoxide plasticizer	20–70
Dialkyl ester of a dicarboxylic acid plasticizer	2–40

12. A closure cap having a vinyl chloride plastisol gasket disposed therein, said gasket having a composition in parts by weight comprising

Polyvinyl chloride dispersion resin	100
Liquid butadiene-acrylonitrile copolymer [1]	1–5
Phenol-formaldehyde copolymer (novolak)	1–5
Polymeric ester epoxide plasticizer	20–70
Dibutyl sebacate	2–40
Titanium dioxide	0.8–1.2
Calcium-zinc stabilizer	0.1–4

[1] Containing from about 20% to about 40% by weight of acrylonitrile in polymerized form.

13. A closure cap having a vinyl chloride plastisol gasket disposed therein, said gasket having a composition in parts by weight comprising

Polyvinyl chloride dispersion resin	100
Liquid butadiene-acrylonitrile copolymer [1]	4
Phenol-formaldehyde copolymer (novolak)	2
Polymeric ester epoxide plasticizer	50
Dibutyl sebacate	4
Titanium dioxide	1
Calcium-zinc stabilizer	0.5

[1] Containing from about 20% to about 40% by weight of acrylonitrile in polymerized form.

References Cited by the Examiner

UNITED STATES PATENTS

2,528,506	11/1950	Foye	260—31.8
2,552,904	5/1951	Newberg	260—32.4
2,614,094	10/1952	Wheelock	260—891
2,659,708	11/1953	Berger et al.	260—31.8

FOREIGN PATENTS

519,991	12/1955	Canada.

OTHER REFERENCES

Buttrey: Plasticizers, Franklin Publishing Co., 1960, pp. 150–152.

MORRIS LIEBMAN, *Primary Examiner.*