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CLOSURE SEALING GASKETS

Charles W. Husum and Jack M. Wheaton, Toledo,
Ohio, assignors to Owens-Illinois Glass Com-
pany, a corporation of Ohio

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The present invention relates to improvements in sealing gaskets which are utilized in conjunction with metal closures in hermetically closing containers, particularly glass containers, for perishable foods.

An object of this invention is the provision of a sealing gasket of such composition as will completely prevent, or in any event reduce to a point at which any deleterious effect is negligible, both corrosion of the metal closure and discoloration of the packaged product.

Both corrosion and discoloration have posed extremely serious problems and resulted in substantial annual loss to the packers, aggregating hundreds of thousands of dollars. With respect particularly to discoloration, many foods, such as beets, squash, carrots, peaches, sweet potatoes, etc., the discoloration (darkening) is quite pronounced, but with practically all products there is some appreciable and objectionable discoloration. Whereas foods sealed with an ordinary standard metal closure become seriously discolored within a given period of time, identical foods sealed with closures incorporating our improved sealing gasket, for the same period of time and under like conditions, show absolutely no discoloration.

It has been quite conclusively determined that entrance of oxygen into the packages is the primary, if not the sole cause of such discoloration. Permeability of conventional sealing gasket compounds to oxygen is the controlling factor with relation to discoloration. We have, as a consequence of the foregoing, determined "GRA," which is butadiene-acrylonitrile rubber, to be most effective in retarding the passage of oxygen into the sealed containers. Butyl rubber has also been found to be satisfactory from permeability standpoint, but is not suitable for use as a gasket because of its lack of resilience.

With respect to corrosion, such occurs in the tin plated closures as a result of very small exposed parts of the iron base material and the creation in effect of an electrolytic cell. Such is due to the existence of an electric circuit through the packed product (which functions as an electrolyte), the sealing gasket, and iron base material beneath the tin coating of the closure.

Our experiments have shown that the part of the carbon filler that has a chain-like structure acts as the cathode and the iron in the closure provides the anode.

Closures of the general type involved are shown in Hoge Patent #2,441,918 and Hohl et al. Patent #2,443,506. Obviously, other types of clo-

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sures may be used. The tin coating almost invariably contains small pinholes, which actually expose the base metal. Organic coatings applied to the plate have weak spots (low dielectric) through which a current will flow. Such conditions, together with the electrical conductivity characteristics of conventional sealing gasket compositions, contributes to the creation of the aforementioned electrolytic cell, and consequent corrosion. As a result there is serious pitting and corrosion of the underside of the closure "panel" or top portion and frequent pinholing. Consequently, food spoilage occurs.

We have discovered, as suggested in our co-pending application, S. N. 237,118, filed July 17, 1951, entitled Method and Means for Inhibiting Corrosion of Metal Closures, that such corrosion can be eliminated by utilizing a gasket formulation, or composition, which limits the percentage of carbon black present with chain-like or electric current conducting structure, as observed under an electron microscope. To this end we have formulated a composition possessing the two-fold function of (1) effectively preventing transfer of oxygen through the gasket to the interior of the container, and (2) preventing an electro-chemical effect. Thus, in a single composition we have provided a structure which eliminates both discoloration and corrosion.

In the sealing gasket which has been found to be most effective, the components, in parts by weight, are about as follows:

GRA-butadiene-acrylonitrile rubber	100
Sulphur	3
Zinc oxide	5
Plasticizer	20
Stearic acid	1
Accelerator	1
Thermax (isolated globule type carbon black particles)	130
Philblack A (chain-type carbon black)	20
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Thermax is a product of Thermatomic Carbon Company and Philblack A, a product of Phillips Chemical Company, Akron, Ohio. The components indicated may be increased, or decreased, slightly, as determined by the physical characteristics desired in the gasket. We have ascertained that "Thermax" which is a carbon black of generally isolated, large globular, or particle structure apparently of about 274 millimicrons

diameter, may comprise from about 125 to 140 parts by weight in a composition of 280 parts. In such carbon black, when compounded into rubber, the globules are sufficiently discrete and isolated from each other to be ineffective in conducting electric current. Such material serves as an excellent filler, but contributes little to the resiliency or hardness of the compound. Any carbon black having the characteristics indicated may be utilized.

With respect to "Philblack A" which is a chain-type carbon black, apparently having a mean particle diameter of about 51 millimicrons, we have determined that it should comprise no more than about 12% by weight of the total composition. This is based upon the discovery that if used in excess, Philblack A, or its equivalent, definitely causes corrosion. This chain-type carbon is a filler which functions to impart smoothness for extrusion purposes, as well as the necessary degree of resilience and hardness. In lieu of Philblack A, we may use in the same amounts any of the following carbon blacks: Statex K. or Statex M., which are furnace blacks produced by Columbian Carbon Company, of New York city; Sterling 30, a product of Cabot, Inc., Boston, Massachusetts; or Dixie 50, or Kosmos 50, which are products of United Carbon Company, Inc., Charleston, W. Va.

We have also discovered that satisfactory results, or in any event, results incomparably superior to those obtained with conventional gaskets, may be obtained where 125 or 140 parts by weight of "Thermax" are used together with 25 or 10 parts by weight of Philblack A, respectively.

As being indicative of the asserted criticalness of the particular carbon content and proportions, we show below three formulations in which the amounts of the two carbons have been varied.

	A	B	C
GRA	100	100	100
Sulphur	3	3	3
Zinc oxide	5	5	5
Plasticizer	20	20	20
Stearic Acid	1	1	1
Accelerator	1	1	1
Thermax	110	125	140
Philblack A	40	25	10

Applicant's several years of experience in the actual testing of processed food closures for resistance to corrosion, or pitting, has developed the fact that the absence of significant pitting, at the end of three months' storage at 125° F., is a reliable index of the performance of closures for one year at room temperature. Quite frequently sheets of tinplate, as received from the tin mill, contain slight pits of from .001 to .003 of an inch in depth. It has also been our observation that a slight etching of the tinplate often occurs, which does not continue after a depth of .001 or .002 of an inch has been reached.

Because of the foregoing we are not concerned with pits of from .001 to .003 of an inch in depth. However, we have discovered that when a pit is in excess of .003 of an inch in depth, after a period of three (3) months' storage at 125° F., that is .004, .005, etc., there is serious danger that corrosion will continue, cause perforation and probable food spoilage.

In the following tables, we have indicated the comparative results of using the three gasket compositions above described. The importance

of controlling the carbon black content is readily apparent.

3 MONTHS—100° F.

Product	Gasket Formula	Caps Examined	Caps with Pits over .003" in Depth
Beets	A	20	3
Do.	B	46	0
Do.	C	46	0
Carrots	A	20	7
Do.	B	44	0
Do.	C	44	0
Liver Soup	A	20	2
Do.	B	46	0
Do.	C	46	0

3 MONTHS—125° F.

Product	Gasket Formula	Caps Examined	Caps with Pits over .003" in Depth
Beets	A	28	6
Do.	B	66	0
Do.	C	67	0
Carrots	A	28	4
Do.	B	65	0
Do.	C	65	0
Liver Soup	A	20	3
Do.	B	45	0
Do.	C	45	0

In all instances, the product color was excellent, thus indicating the impermeability of the selected type of rubber to atmospheric oxygen and that discoloration is caused by entry of oxygen into the container. Corrosion, however, was excessive in formulation A. By contrast, the modification of the carbon content in formulations A and B, wherein Thermax was increased and Philblack A decreased, there was no ultimate corrosion deeper than .003 of an inch.

It has been determined that the best results, as regards non-corrosive action, are obtained where the ratio of Philblack A to Thermax is less than about 4 to 11.

Thus, it is apparent that we have discovered that corrosion and discoloration are not inter-related as regards cause, in that either can be present without the other. Also, that permeability of the gasket material to oxygen determines the extent and rapidity of discoloration and that the carbon black content and type, determine whether corrosion will, or will not develop, quite apart from the discoloration aspects. It is possible to concurrently have severe corrosion of the closure and good color retention, such being due to the use of the proper type of rubber, but improper carbon blacks and in the wrong proportions. Moreover, both corrosion resistance and poor color retention may result, if the rubber component is incorrect. In our gasket composition both of the foregoing problems have been completely solved.

Inasmuch as some foods are much less subject to discoloration than others and in such instances only corrosion prevention requires special attention, we contemplate the use of known types of rubber which may be less effective than GRA as a barrier to oxygen passage. However, the use of Thermax or equivalent carbon blacks such as "Shell 53," is essential in corrosion prevention. Hence in such circumstances we utilize these two carbon blacks in about the proportions stated heretofore, it being understood that Philblack A serves to improve workability, extrusion, etc., of the composition, as explained above.

Modifications may be resorted to within the spirit and scope of the appended claims.

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We claim:

1. A sealing gasket composition for sheet metal caps used in closing bottles and jars, which comprises about 100 parts butadiene acrylonitrile rubber; about 3 parts sulphur; about 5 parts zinc oxide; about 20 parts plasticizer; about 1 part stearic acid; about 1 part accelerator; about 130 parts of carbon black composed largely of discrete isolated particles and about 20 parts of a chain-like carbon black.

2. The composition recited in claim 1, wherein furnace type carbon black is the chain-like carbon black.

3. The composition recited in claim 1, wherein the chain-type carbon black constitutes a maximum of about 12% by weight of the total composition.

4. A sealing gasket composition for sheet metal caps used in closing bottles and jars comprising 100 parts by weight of butadiene-acrylonitrile rubber, from about 25 to about 10 parts by weight of a carbon black of chain-like structure and from about 125 to about 140 parts by weight of a carbon black composed of isolated globular particles.

5. A sealing gasket composition for sheet metal caps used in closing bottles and jars comprising butadiene acrylonitrile rubber and a filler

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consisting of a carbon black which is composed largely of substantially discrete, relatively isolated particles and a carbon black having a chain-like structure, the ratio of the second named carbon black to the first named carbon black being less than 4 to 11 and the carbon black of chain-like structure comprising less than about 12% by weight of the total composition.

6. A sealing gasket composition for sheet metal caps used in closing bottles and jars comprising butadiene acrylonitrile rubber, a carbon black of chain-like particle structure, and a carbon black consisting largely of substantially discrete relatively isolated globular particles whose diameter is approximately 274 millimicrons, the ratio of the carbon black of chain-like particle structure to the second named carbon black being less than 4 to 11 and the carbon black of chain-like structure comprising less than about 12% by weight of the total composition.

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