METHOD AND APPARATUS FOR PROCESSING HIGH NITRILE POLYMERS

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Filed: Nov. 11, 1971

Appl. No.: 197,766

U.S. Cl. 34/12, 34/28, 209/11

Int. Cl. F26b 7/00

Field of Search 209/473; 34/60, 12, 17, 34/22, 28, 132, 134; 209/11, 471-473, 134, 135, 152

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ABSTRACT

A method of preparing a high nitrile molding resin for conversion into articles for packaging environmentally sensitive materials which involves mixing a moisture-containing batch of such resin having a relatively broad particle size distribution range within a stationary, heated processing chamber without mastication and without subjecting the particles to any substantial back pressure, the major constituent of such resin being a polymerized monomer selected from the group consisting of acrylonitrile, methacrylonitrile and mixtures thereof, and forcing low pressure gas through the chamber while the mixing continues, to purge the vaporized moisture and entrain a fines portion of the particles out of the chamber. In a preferred form of mixing, continuously rotating plows force portions of the particles upwardly along and in contact with the heated chamber surface in a converging mixing pattern while other portions are diverted out of such a pattern by means of plates rotating with the plows so as to increase the exposed surface area of individual particles.

8 Claims, 3 Drawing Figures
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CROSS REFERENCES TO RELATED APPLICATIONS

2. Serial No. 72,237 now abandoned, filed Sept. 14, 1970, entitled "Process For Preparing Articles of Improved Color From Nitrile Polymers."
4. Serial No. 140,588 now abandoned, filed May 5, 1971, entitled "Plastics Packages For Comestibles."

BACKGROUND OF THE INVENTION

This invention relates to high nitrile polymers for packaging environmentally sensitive materials and more particularly to a method and means for processing such polymers preliminary to extrusion.

As brought out in U.S. Pat. Nos. 3,426,102 and 3,451,538, thermoplastic polymers wherein the major constituent is a polymerized nitrile-group-containing monomer such as acrylonitrile, methacrylonitrile and mixtures thereof, are known in the prior art as highly desirable for packaging environmentally sensitive products such as foodstuffs, comestibles, medicines, cosmetics and other related substances, in view of the extremely good oxygen and carbon dioxide barrier properties and general inertness to the packaged contents exhibited by these materials. In addition, the use of such polymers for packaging carbonated beverages including soft drinks and beer is brought out in the above cited and pertinent applications, all of which are assigned to the present assignee. Thus, it is known to overlap such products in film or sheet made of these materials and/or to package such products in containers molded from such polymers.

Immediately after polymerization, such high nitrile polymers are generally (though not necessarily) in the form of a slurry of beads suspended in water which is usually centrifuged to remove the bulk of the water leaving a wet cake having a moisture content of from about 5 to 6 weight percent. The cake is then dried, e.g., in a rotary dryer, to reduce the water level to some 0.3 to 1.7 weight percent.

These polymers, however, are quite hygroscopic due to their polar nature and accordingly will absorb moisture if exposed to a humid atmosphere. Such absorbed moisture, if excessive, will appear as unsightly bubbles in the polymer extrudate, and consequently it has been necessary in the past to dry the polymer again prior to extrusion if it has been exposed to the atmosphere in the interim or alternatively to protect it from exposure to humidity after once drying it.

Such high nitrile polymers, especially wherein the major constituent is polymerized methacrylonitrile, tend to be rather heat sensitive when exposed to relatively high temperatures for prolonged periods of time. Under such circumstances, these polymers tend to partially break down into the monomer(s) from which they were generated, and in so doing, the polymer undesirably turns to a yellow color, the extent being dependent on the severity of the heat exposure. Also, the monomer thus generated is absorbed into the remaining polymer and after such polymer has been converted into an article such as a container into which an environmentally sensitive product has been placed, it has been found that the thus absorbed monomer when present in relatively large concentrations can bleed out of the polymers into the packaged product, thus undesirably contaminating it. As typically disclosed in application Ser. No. 72,237, it has unexpectedly been found that the presence of water during extrusion of such high nitrile polymers tends to improve both the color and the integrity of the extruded product. However, the water level in the polymer feed to the extruder under such circumstances is rather critical, since if it is excessive, as mentioned above, bubbles will appear in the extrudate, whereas if it is insufficient the benefits achievable therefrom will not be realized.

In addition, as disclosed in aforementioned application Ser. No. 179,583, entitled "Improved Method Of Forming A Plastic Container For Carbonated Beverages," filed Sept. 10, 1971, when high nitrile polymers are fabricated into containers such as bottles and filled with a carbonated beverage such as a cola soft drink, it has been found that after a relatively brief period comparable to the normal shelf life of a carbonated beverage, the bottles tend to crack and fail at temperatures on the order of 90° to 100°F. If the concentration of unusually small particles in the extruder feed had been excessive. Such fines when interspersed with coarser particles also tend to interfere with homogeneous mixing of the melt in the extruder. For example, the clearance between the outer surface of the extruder screw flights and the inner surface of the extruder barrel may be somewhat greater than the nominal size of these fines, thus providing an area where such fines can collect and, under the influence of the extruder back pressure, periodically flow backward in the opposite direction from that of extrusion, thus causing extruder surging.

Furthermore, such high nitrile polymers though possessing extremely effective barrier and strength properties are relatively brittle and noticeably deficient in impact resistance when molded into articles, the latter property being rather important when the formed product is a container such as a bottle or a can which will be exposed to rather severe handling conditions e.g., during filling and subsequently by a purchaser. A known way to improve such impact resistance, as set forth in aforementioned Ser. No. 171,341, is to blend the high nitrile barrier polymer with an impact modifying material, and this is preferably done for the aforementioned reason without substantially increasing the heat history of the material.

The necessity of further refining high nitrile resins subsequent to polymerization and prior to extrusion therefore is desirable.

In the past, methods of processing such high nitrile polymers have required a series of separate processing steps and separate equipment components to carry out the drying, fines removal and impact modifying of the polymers. In addition, it was extremely difficult to
avoid overdrying the resin, and also the time necessary to achieve the desired moisture level was on the order of 24 hours, even after the polymer had been once dried and subsequently merely exposed to normal surroundings. High intensity mixers have been used to blend impact modifiers with high nitrile resins upstream of the extruder, but this results in substantial fusion of the particles together and in an increase in the heat history of the materials because of the high shear rates involved. Vacuum ovens have also been tried, however moisture control is difficult, the cycle times again are excessive since there is no motion of the resin during drying, and the fines must be removed and impact modifiers blended separately.

**SUMMARY OF THE INVENTION**

Now, however, there has been discovered a new technique for processing high nitrile polymers subsequent to polymerization and prior to extrusion which overcomes the previously mentioned difficulties of the prior art.

Accordingly, it is a principal object of this invention to provide an improved technique for preparing a molding resin preliminary to extrusion wherein the major constituent thereof is a polymerized nitrile-group containing monomer.

An additional object of this invention is to provide an improved method of controlling the moisture content of high nitrile polymers in bead form.

A further object of this invention is to provide an improved versatile method of blending impact modifiers into high nitrile resins without substantially increasing the heat history of the resins.

Yet another object of this invention is to provide an improved technique for removing fines from a high nitrile molding resin which is to be converted into a container for holding a pressurized environmentally sensitive material.

Another object of this invention is to provide a method of simultaneously carrying out the drying and blending of, and fines removal from a molding resin wherein the major constituent is a polymerized monomer selected from the group consisting of acrylonitrile, methacrylonitrile and mixtures thereof.

A further object of this invention is to provide an improved means for carrying out the above objects.

Other objects of this invention will in part be obvious and will in part appear hereinafter.

These and other objects are accomplished by providing a method of preparing a molding resin for conversion into articles for packaging environmentally sensitive materials which comprises mixing a moisture-containing batch of thermoplastic resin in particle form having a relatively broad size distribution range within a heated stationary processing chamber without mastication and without subjecting the particles to any substantial back pressure in order to vaporize the moisture, the major constituent of the resin comprising polymerized nitrile monomer selected from the group consisting of acrylonitrile, methacrylonitrile and mixtures thereof, and forcing low pressure gas through the chamber while the mixing continues in order to purge the vaporized moisture and entrain a fines portion of the particles out of said chamber.

Preferably, the resin is in bead form and the polymerized nitrile monomer is present at a level of from 55 to 98 weight percent in the resin, the remainder of the resin comprising at least one ethylenically unsaturated non-nitrile-group containing copolymerized monomer, preferably styrene.

In a preferred form of mixing, continuously rotating plows within the processing chamber advance into the particles to repeatedly force substantial portions thereof upwardly along the surface of the processing chamber to establish a converging mixing pattern while vaporizing at least a portion of the moisture, while plates rotating with and inside the plows direct portions of the resin out of the converging pattern, thus increasing the exposed surface area of individual particles in order to improve the effectiveness of the purge-entricing gas. The mixing and gas flow are terminated when the moisture in the polymer is reduced to a level of from 0.06 to 2.0 and preferably from 0.06 to 0.15 weight percent of the polymer present in the chamber.

When feed to the processing chamber is in the form of polymer beads ranging in size from 0.0035 to 0.035 inch, the particle size of the major proportion of the beads entrained out of the chamber with the gas is less than 0.007 inch (80 mesh). The level of the fines in the processing chamber is reduced to one which will not give problems in subsequent extrusion and container performance when the gas is allowed to pass through the chamber for a period of from 60 to 180 min. while the plows and blades rotate at from 100 to 200 r.p.m.

An impact modifier, which preferably is the product in crumb form of a graft polymerization onto a rubber of methacrylonitrile and at least one mono-vinylidene aromatic compound, may be blended with the high nitrile polymer in the processing chamber. To accomplish this, the crumblike modifier is brought into intimate contact with separately rotating high shear impellers within the processing chamber for a limited time to reduce the crumb to powder form, whereupon the bead material is thereafter mixed in the chamber with the powder as previously mentioned such that the beads are coated with the impact modifier in a manner which facilitates good dispersion of the modifier in the matrix polymer during subsequent melt extrusion.

The apparatus includes a jacketed, stationary, cylindrical processing chamber having gas inlet and outlet ports, plows and blades mounted on rigid arms extending radially of a rotatable central shaft, means for forcing purge gas through the chamber as the plows and blades rotate, means for controlling the moisture content and temperature of the purge gas and separating means downstream of the chamber to remove the fines from the gas.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In describing the overall invention, reference will be made to the accompanying drawing wherein:

FIG. 1 is a vertical, schematic, pictorial view with parts broken away of apparatus for carrying out the process of the present invention;

FIG. 2 is a partial view similar to FIG. 1 of an alternative form of apparatus useful in the process of the present invention; and

FIG. 3 is a graph illustrating a typical particle size distribution curve of material processed with the apparatus of FIG. 1.
DETAILED DESCRIPTION OF THE ILLUSTRATED EMBODIMENTS

Referring now to the drawing, there is shown in FIG. 1 an apparatus 10 for processing a molding resin for conversion into articles for packaging environmentally sensitive materials. Apparatus 10 includes a stationary, horizontally oriented elongated cylindrical processing chamber 12 the limits of which are defined by surface 14. Unit 12, including its internal components to be more completely described hereafter, is a modified version of commercially available Roto Plas horizontal unit, Model K-2400, manufactured by Littleford Bros. Inc., 4141 Airport Rd., Cincinnati, Ohio, 45226. Outer wall 15 of chamber 12 is substantially completely surrounded by jacket 16, thus forming annular space 17 between wall 15 and jacket 16 for circulation of a heating medium, to be described more completely hereafter.

Horizontal shaft 18 extends through chamber 12 on the central axis thereof and is connected to any conventional drive means for imparting rotary motion thereto, (not shown) such as a gear reducer or electric motor.

A series of spaced, radially extending supporting arms 20 are secured to shaft 18 along the length thereof, the location of each being important to ensure that the material being processed is properly distributed throughout chamber 12 in a manner to be described hereafter in more detail. Arms 20 have mixing elements thereon comprising, in the embodiment of FIG. 1, a plow 22 positioned at the extremity of each arm 20 close to yet incrementally spaced from surface 14 of processing chamber 12, and a blade 24 of approximately the same surface area as a plow 22 angularly mounted with respect to the axis of arm 20. Each plow 24 is basically a section of a hypothetical spiral like ribbon which, if present in its entirety, would wind around chamber 12 adjacent surface 14, and consequently, the orientation of any individual plow along the length of chamber 12 should be strictly maintained to preserve this pattern. Likewise, the angular relationship of each plate 24 to its particular plow 20 is important to achieve the desired mixing distribution, and consequently, one plate should not be interchanged with another on a different arm.

Gas inlet port 26 and outlet port 28 are provided above and preferably at an angle of between 30° to 60° to the axis of chamber 12. Means such as fan 30 are provided for forcing low pressure air into chamber 12 through port 26 and out of chamber 12 through port 28. A suitable conventional valve mechanism, not shown, such as a damper plate may be provided between the discharge of fan 30 and inlet port 26 to adjust the flow of air to chamber 12. Means such as a coil 32 may be mounted in the conduit connecting the discharge of fan 30 to inlet port 26 to regulate the temperature of the air such that its moisture content is lower than that in chamber 12. Either a low or high temperature heat transfer medium may be passed through coil 32 by conventional means, not shown, depending on whether it is desired to heat or cool the air passing through chamber 12. For example, when the water content of the air entering fan 30 is high such as occurs during humid summer conditions, a refrigerant may be circulated through the initial portion of coil 32 to reduce the water level of the air while a heating medium is circulated through the final portion of the coil to increase the temperature of the reduced water level air before entering chamber 12. However, if it is found that the moisture level in the resin is too low, the significance of such a situation being more completely described hereafter, it is possible to alter this procedure to increase the humidity of the air over that already in chamber 12.

Apparatus 10 also includes means for circulating a heating medium through annular space 17 between jacket 16 and wall 15 of chamber 12 to increase the temperature of surface 14. These means may include a conduit 34 connected to a suitable source of low pressure steam and to jacket 16 opposite space 17, having valve V mounted therein, and a discharge conduit 36 having a self-actuating condensate trap T installed therein. A suitable conventional cooling system, not shown, may also be used with space 17 in order to reduce the temperature of surface 14 should it undesirably rise to an excessive temperature during operation of the system.

Means such as separator 38 may be provided downstream of chamber 12 having a series of spaced baffles 41 mounted therein and inclined at an angle of about 45° to minimize entrainment of large polymer particles with the entraining gas. Also, means such as a porous fabric sleeve member 40 or a cyclone separator may be provided downstream of separator 38 to remove the fines portion 42 from the entraining air prior to discharge of the latter to the atmosphere, or, in a closed loop system, prior to recycle back through temperature conditioning means 32.

Apparatus 10 also includes a conventional feed inlet port 44 and refined product discharge port 46 communicating with chamber 12. A well extending into chamber 12 containing temperature sensing means such as a thermocouple (not shown) may be provided for measuring the stock temperature during processing.

When it is desired to blend the high nitrile polymer with an impact modifier, a series of high speed impellers 58 are provided which are equally spaced from each other along the length of chamber 12 and which protrude into chamber 12 a short distance below its longitudinal axis. In the illustrated embodiment, each four bladed impeller is mounted on a shaft associated with conventional rotary drive means such as a motor operating at 3,500 r.p.m.

In the apparatus embodiment illustrated in FIG. 2, the plow and plate members are integrally formed as single, one piece, pie shaped members 48 each of which is situated at the outer end of an arm 50 which is otherwise positioned similarly to arm 20 of the apparatus of FIG. 1. Pie shaped member 48 includes a plow portion comprising triangular surface 52 and a plate portion comprising surface 54 gradually tapering inwardly and upwardly from edge 56 at the junction between surfaces 52 and 54. The low pressure air, separating and high shear mixing components of the system illustrated in FIG. 1 may also be used with the apparatus of FIG. 2. A modification, is available commercially from the aforementioned Littleford Bros. Inc. and is known as Roto-Plas unit, Model FM130.

In operation, valve V is initially opened to allow low pressure steam to flow into annular space 17 in order to increase the temperature of surface 14 of chamber 12 to approximately 190°-200° F., though somewhat
higher temperatures could be used. It should be real-
ized, however, that it may be possible to entirely elimi-
nate heating in space 17 or, alternatively, to eliminate it 
until part way through the drying process, especially 
when the purge and entraining air is well heated by coil 
32, as more completely described hereafter. The drive 
mechanism is then actuated to cause shaft 18, arms 20, 
plows 22 and plates 24 to rotate at 150 r.p.m. within 
chamber 12. A speed of from 100 to 200 r.p.m. has 
generally been found acceptable in processing the high 
nitrile polymers of the present invention. At rotary 
speeds above 200 r.p.m., substantial undesirable fusion 
occurs when processing high nitrile polymers, whereas 
at speeds below 100 r.p.m., movement of the particles 
within the chamber is substantially diminished and pro-
cessing time accordingly, lengthened. A suspension po-
lymerized thermoplastic batch of a high nitrile content 
resin in bead form is then introduced into chamber 12 
through inlet port 44. The distribution of the resin 
beads of the batch range in size from 0.0035 to 0.035 
inch (Tyler), with a screen analysis thereof depicted by 
the curved labeled "CONTROL" in FIG. 3. The batch 
fed to chamber 12, in the present instance, was a resin 
comprising 90 weight percent polymerized methacrylo-
nitrile and 10 weight percent polymerized styrene hav-
ing a moisture content of about 5 to 6 weight percent, 
which represents the typical level of water remaining 
after a suspension polymerized slurry of such beads has 
been passed through a centrifuge. It should also be real-
ized, however, that resin may also be processed accord-
ing to the method of the present invention which has 
a considerably lower water content, e.g., from 0.3 to 
1.7 weight percent, such as that representing water ab-
sorbed by the hygroscopic material when in equilib-
rium with the surrounding atmosphere. The time pe-
riod during which such a material is present in chamber 
12 is merely reduced to compensate for the lower water 
level in the feed.

After the batch has been charged to chamber 12, fan 
30 is energized and the conventional regulating valve, 
not shown, adjusted to allow passage of some 60 to 90 
cfm. of air preferably at a temperature of 180°-220°F. 
to flow into chamber 12 through inlet port 26. 
The amount of material charged to chamber 12 should 
be obviously considerably more than that de-
picted in the drawing, e.g., the volume of chamber 12 
should be filled to from 50 to 75 percent of capacity, 
FIG. 1 being simplified in order to schematically better 
depict the action of the various mixing elements on 
the bead charge. Since the temperature of surface 14 is 
relatively low in comparison with that necessary to fuse 
the polymer stock, and since shaft 18 and the various 
mixing elements attached thereto is turning relatively 
slowly at 150 r.p.m., frictional heat is kept to a mini-

mum and maceration (size reduction) of the beads to 
any substantial extent accordingly does not occur. 
Some slight build up of material on the surface of the 
beads adjacent hot surface 14 can occur over a period 
of time. Pressure is likewise kept to a minimum, the 
maximum pressure in chamber 12 being on the order of 
5 psig., this representing the pressure drop between 
outlet port 28 and the downstream side of sleeve mem-
ber 40.

As shaft 18 rotates in the counterclockwise direction 
of the arrow in FIG. 1, each continuously rotating, an-

gularly positioned plow 22 is advanced into the sub-

stantially spherically shaped beads in order to repeat-
edly force portions thereof in front of the plows up-
wardly along and in contact with the adjacent, elevated 
temperature surface 14 of chamber 12, thus vaporizing 
the surface moisture which usually amounts to about 
85 percent of that present, and over a period of time, 
driving internal moisture to the surface to permit such 
vaporization to occur. Continuous movement of plows 
22 repeatedly quickly moves the material away from 
heat exchange surface 14 in a scouring fashion so that 
additional material will be exposed. In addition, due to 
the angular position of plows 22, a basic converging 
mixing pattern will be established within chamber 12.

More particularly, when shaft 18 is turning in the direc-
tion indicated in FIG. 1, the material in chamber 12 to 
the left of a vertical center line through its axis will be 
moving toward such vertical line following the contour 
of chamber 12, or in the direction of arrows 19. Mate-

tial to the right of such vertical line will be moving in 
the opposite direction toward such vertical center line 
in the direction of arrow 23, due to the particular angle 
of the plows in the right side of the apparatus. Thus, a 
mixing pattern converging toward the center of cham-
ber 12 will be established by plows 22. Blades 24, how-
ever, are oriented at such an angle that they will divert 
portions of the thus moving beads out of this pattern in 
the opposite direction and back toward the end walls of 
chamber 12 as exemplified by arrows 21 on the left of 
the vertical centerline and arrows 25 to the right of 
such centerline. Such blade action tends to individu-
alyze or separate the particles from each other, thereby 
tremendously increasing their surface exposure and 
minimizing any tendency for fusion to occur. Such indi-

vidualization of the particles serves to better expose 
them to the vaporizing effect of the elevated tempera-
ture air passing through the chamber, and probably 
more importantly, such continuous random movement 
renders a fines portion of the beads having a particle 
size at the low end of the aforementioned distribution 
range more susceptible to entrainment in the air in 
order to remove such fines from chamber 12 through 
outlet port 28 as plows 22 and blades 24 continue to ro-
tate. Obviously, the vaporized moisture is also purged 
from chamber 12 at the same time.

Impellers 28 may optionally be energized for a lim-
itted time, e.g., on the order of from 5 to 15 minutes, 
part way through the drying/classifying cycle, if the 
temperature of the mixing beads is kept sufficiently 
low, e.g., on the order of 110°F. Such action of the im-

pellers serves to further centrifugally force the beads 
against the heated chamber wall, as well as to improve 
blend uniformity and fines separation.

After a period of some 60 minutes, a sample is extri-
cated from chamber 12 through discharge port 46 into 
a dry container properly covered to avoid moisture 
pickup. The sample is then compression molded into 
a disc which is then compared with a control disc previ-
ously molded from the same composition, but which 
was at the desired moisture level as 0.08 weight percent 
on molding. The size and number of bubbles in the 
sample is then visually compared with the control, and 
if such a comparison indicates that the sample is as dry 
and preferably somewhat dryer than the control, the 
batch is ready to be discharged from chamber 12. If in-
idications are that the moisture level in the sample is too 
high, drying is allowed to proceed for some fifteen ad-
ditional minutes and the just mentioned test preformed 
again. This test procedure is repeated until indications
are that the batch is at the desired moisture level, i.e., having a water content of from 0.3 to 1.7 weight percent. When using the apparatus arrangement of FIGS. 1 and/or 2, for high nitrile polymers in bead form having a moisture content of between 0.06 to 0.12 weight percent, blow and blade movement of between 100 to 200 r.p.m., and from 60 to 90 cmf. of air at a temperature from 170° to 230°F., the time necessary to reduce the moisture content of the batch to 0.06 to 0.12 weight percent is between 60 to 180 minutes. The resin is then discharged from chamber 12 through port 46 and introduced to the feed end of a conventional extruder without being further exposed to a humid environment. The batch is homogeneously mixed under pressure in the extruder and forced through an annular die at a temperature of some 400° to 500°F. in the form of a tubular parison. The parison may then be conventionally enclosed in a hollow blow mold and expanded outwardly against the walls of an internal cavity therein to form a hollow article.

With respect to the fines portion of the batch entrained out of chamber 12 by the air, a screen analysis of the material collected in sleeve member 40 indicated, as illustrated in FIG. 3, that the major proportion thereof (i.e., on the order of 70 weight percent) passes through an 80 mesh Tyler screen size which corresponds to 0.007 inch in size. Since some 13 weight percent of the feed to chamber 12 (“CONTROL” in FIG. 3) passed through 80 mesh, this screen analysis indicates a 51 weight percent increase in the level of “through” 80 mesh beads entrained out of chamber 12 over that initially charged thereto. This fines portion after removal from sleeve 40 was then separately fed to a pelletizing extruder wherein the fine beads were compacted into larger cubical pellets, portions of which were then fed with subsequent batches of resin processed in chamber 12 into the previously mentioned article-forming extruder. It should also be realized that high nitrile polymers in forms other than substantially spherically shaped beads, e.g., cubical pellets or other different shapes may also be processed in chamber 12 if the moisture level thereof has risen above that desirable for acceptable melt processing.

In another experiment, an impact modifier was prepared comprising a graft copolymer of polymerized methacrylonitrile and styrene onto a 75/18/7 weight percent butadiene/methacrylonitrile/styrene terpolymer rubber wherein the rubber constituted 40 weight percent of the graft copolymer. This impact modifier in crumb form was first charged to chamber 12 and impellers 58 energized for a period of 30 minutes to reduce the crumb-like material to powder form, whereupon the powdered material was removed from chamber 12. A wet batch of 90/10 weight percent polymerized methacrylonitrile/styrene in bead form was then charged to chamber 12 in the manner previously described, the moisture content thereof being at a level of 0.5 weight percent water. The water was reduced to a level of 0.08 weight percent in the manner previously described whereupon a sufficient quantity of the powdered impact modifier was returned to chamber 12 such that the content of the mixture therein was 90 weight percent polymerized methacrylonitrile/styrene beads - 10 weight percent impact modifier. Shaft 18 was again rotated and surface 14 was not heated to elevated temperature and fan 30 was deenergized so that no air passed through chamber 12.

After a mixing period of about some 60 min., the bead material was found to be well coated with the powdered modifier, and ready for extrusion and blow molding into a container having improved impact resistance. Obviously alternative sequencing of the mixing steps are workable, e.g., the bead material could be processed prior to the crumb or alternatively, under certain conditions it may be possible to dry and classify the beads simultaneously with coating by the impact modifier.

In the embodiment of the invention illustrated in FIG. 2, the action of members 48 at the outer end of each arm 50 is essentially the same as that of plows 22 and blades 24 of the apparatus of FIG. 1. The beads are forced upwardly along the surface of the chamber to promote heat transfer for vaporizing the moisture while being forced in opposite directions in a converging pattern, arrows 29 representing one direction in FIG. 2. Surfaces 54, however, serve to deflect portions of the material back in the opposite direction away from the center of chamber 12 in the manner previously described, so as to individualize and separate the particles from each other to improve entrainment of the fines portion out of the processing chamber.

The above description and particularly the drawings are set forth for purposes of illustration only and are not to be taken in a limited sense.

With respect to extrusion of the type of high nitrite polymers of concern in the present invention, as previously mentioned, water has been found to effectively reduce the extent to which the polymers decompose and has also been found to be effective in lowering the viscosity of the polymer during melt processing. As also indicated, however, if the water level in the polymer exiting from the extrusion orifice is too high, e.g., in excess of 0.15 weight percent, undesirable water bubbles will appear. However, if the water is removed from the polymer immediately upstream of the extrusion outlet, e.g., by vacuum venting, it may be possible to utilize the water to maximum advantage while avoiding bubble generation. Under such conditions, it may even be desirable to add water to the processing chamber of the present invention such that it is present in the extruder feed at a concentration of as much as two weight percent, or alternatively to control the water level in a batch initially having more than two percent water such that it is at this latter level on being discharged from chamber 12. Regulating the humidity of the purge gas such that its water level is greater than that in the processing chamber is another convenient way of adding moisture to the material.

Typical of the nitrile monomers suitable for use in making the polymer processable according to the present invention are, for example acrylonitrile, methacrylonitrile, ethacrylonitrile, propacrylonitrile, alpha-chloro-acrylonitrile, alpha-bromoacrylonitrile, alpha-fluoroacrylonitrile, fumarodinitril, maleodinitril alpha-cyanostyrene, vinylidene cyanide, alpha-cyano acrylic acids, alpha-cyano acrylates such as alpha-cyano methyl acrylates, alpha-cyano ethyl acrylates, and the like, 2, 3-dicyanobutene-2, 1, 2-dicyano propane-1, alpha-methylene glutaronitrile, and the like. The preferred monomers for this purpose are acrylonitrile, methacrylonitrile, and mixtures thereof. The preferred level of polymerized nitrite monomer in the polymer is from 55 to 98 weight percent.
Theoretically any monomer or monomers which are copolymerizable with the nitrile group containing component of the polymer, assuming they would not impart undesirable properties to the finished product, may be employed in the practice of this invention. Such a co-monomer is desirable, though not necessarily, present for the purpose of improving melt processability of the thermoplastic, since if there is an excess of CN groups in the polymer, the material exhibits a relatively high degree of polarity and the backbones tend to become attracted to each other, thereby reducing the melt processability characteristic of the polymer. The co-monomer tends to reduce this tendency but not sufficiently so as to substantially diminish the barrier properties. This co-monomer may be present in the polymer at a level of from 2 to 45 percent by weight. Examples of such monomers are ethylenically unsaturated aromatic compounds such as styrene, alpha-methyl styrene, ortho-, meta-, and para-substituted alkyl styrenes, e.g., ortho-methyl styrene, ortho-ethyl styrene, para-methyl styrene, para-ethyl styrene, ortho-, meta-, or para-butyl styrene, ortho-, meta-, or para-secondary butyl styrene, ortho-, meta-, or para-tertiary butyl styrene, etc., alpha-halogenated styrene, e.g., alpha-chlorostyrene, alpha-bromostyrene, ring-substituted halogenated styrenes, e.g., ortho-chloro-styrene, para-chlorostyrene, and the like; esters of ethylenically unsaturated carboxylic acids e.g., methyl acrylate, methacrylate, ethyl acrylate, ethyl methacrylate, esters of acrylic acid, methacrylic acid, propionic acid, crotonic acid, and the like. Vinyl esters, e.g., vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, etc.; vinyl and vinylidene halides, e.g., vinyl chloride, vinyl bromides, vinylidene chloride, vinyl fluorides, etc.; vinyl ethers, e.g., methyl vinyl ether, ethyl vinyl ether, propyl vinyl ether alpha-olefins, e.g., ethylene, propylene, butene, pentene, hexene, heptene, octene, isobutene, and other isomers of the foregoing.

This invention also contemplates the use of up to 20 percent by weight and preferably from 0 to 15 percent by weight of impact modifying materials which are compatible with the high nitrile based polymer of the invention. The proportion of such materials when considered with the level of non-nitrile-group containing material in the polymer should not be allowed to exceed 25 weight percent and preferably not allowed to exceed 15 weight percent if radical shifts in property levels are to be avoided. Typical impact modifiers which may be blended with the polymer of the present invention are synthetic or natural rubber components such as, for example, polybutadiene, butadiene-styrene copolymers, isoprene, neoprene, nitrile rubbers, acrylate rubbers, natural rubbers, interpolymers of butadiene with acrylonitrile, methacrylonitrile tertiary butyl styrene, styrene and mixtures thereof such as acrylonitrile-butadiene copolymers, methacrylonitrile-butadiene copolymer, acrylonitrile-styrene-butadiene terpolymers, methacrylonitrile-styrene-butadiene terpolymers, methacrylonitrile-tertiarybutyl styrene-butadiene terpolymers, acrylonitrile-tertiarybutyl styrene-butadiene terpolymers, ethylene-propylene copolymers, chlorinated or fluorinated rubbers, etc. This rubbery component may be incorporated into the polymers of this invention by any of the methods which are well known to those skilled in the art, e.g., direct polymerization of monomers, polyblends, grafting the monomer mixture onto the rubbery backbone, physical admixture of the rubbery component, etc. Other tough polymers, not considered or known as rubber based materials may be used as impact modifiers. These include polycarbonate, polyethylene, polyethylene/vinyl acetate, polyethylene/vinyl alcohol, polyamides, polyketones, phenoxies, polyacetals, and silicones.

This invention also contemplates the use of conventional additives such as dyes, fillers, pigments, plasticizers, stabilizers, processing aids, etc. in the high nitrile polymer refining process of this invention.

Various modifications and alterations will be readily suggested to persons skilled in the art. It is intended therefore, that the foregoing be considered as exemplary only and that the scope of the invention be ascertained from the following claims.

What is claimed is:

1. A method of processing a molding resin for conversion into articles for packaging environmentally sensitive materials which comprises:
   a. advancing plows continuously rotating within a heated cylindrical processing chamber in a direction circumferential to the longitudinal axis of said chamber into a moisture-containing batch of a high nitrile thermoplastic resin in particle form situated therein to establish a converging mixing pattern and to repeatedly force portions of the batch upward along the surface of the chamber while vaporizing at least a portion of said moisture, said particles having a relatively broad size distribution range;
   b. diverting portions of the resin in substantially the opposite direction from said converging pattern to increase the surface exposure of said particles without substantially fusing them together;
   c. rotating a series of impellers on shafts extending toward said axis at a speed greater than said plows to centrifugally disperse the resin particles in said chamber while continuing movement of said plows;
   d. forcing low pressure gas through said thus moving particles to purge the vaporized moisture and to entrain a portion only of said particles having a size at the low end of said distribution range from said chamber.

2. A method of processing a molding resin to be converted into articles for packaging environmentally sensitive materials which comprises:
   a. feeding a moisture-containing thermoplastic resin in bead form having a relatively broad size distribution range to a cylindrical processing chamber, the surface of which is at elevated temperature, said resin comprising polymerized nitrile monomer selected from the group consisting of acrylonitrile, methacrylonitrile and mixtures thereof and at least one ethylenically unsaturated non-nitrile group containing copolymerized monomer, said polymerized nitrile monomer constituting from about 55 to 98 weight percent of the resin;
   b. advancing plows continuously rotating within said chamber in a direction circumferential to the longitudinal axis thereof into said beads to establish a mixing pattern within the chamber converging toward a plane central and perpendicular to said longitudinal axis and to repeatedly force substan-
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13. Partial portions of said beads upwardly along the elevated temperature chamber surface to vaporize at least a portion of said moisture;

c. diverting portions of the beads in the opposite direction from said converging pattern with plates continuously rotating with said plows to increase the surface exposure of said beads without substantially fusing them together; and

d. forcing low pressure gas through said thus moving beads to purge the vaporized moisture and to entrain only a portion of said beads having a particle size at the low end of said distribution range from said chamber.

3. The process of claim 2 wherein steps (b), (c) and (d) continue for a period of at least 90 minutes.

4. The process of claim 2 wherein the advancing movement of the plows is terminated when the moisture is reduced to a level of from 0.06 to 0.12 weight percent of the beads in the chamber.

5. The process of claim 4 wherein the moisture content of the bead feed to the processing chamber is between 0.3 to 1.7 weight percent water.

6. The process of claim 2 wherein the particle size of the beads fed to the chamber is between 0.0035 to 0.035 inch and the size of the major proportion of the beads entrained out of said chamber with the gas is less than 0.007 inch.

7. The process of claim 2 wherein said plows and blades are rotating at a speed of from 100 to 200 r.p.m.

8. In apparatus for processing a molding resin for the production of plastic articles which includes a jacketed, elongated, horizontally oriented stationary, cylindrical processing chamber, a rotatably mounted shaft on the longitudinal axis of said chamber having spaced rigid arms thereon, said arms having plows at their outer ends adjacent the surface of the processing chamber for moving said resin along said surface as the shaft rotates, said plows being shaped also so as to move said resin in a direction along said axis toward the center of the chamber, and a series of mixing impellers on shafts extending into the chamber through the wall thereof toward, below and spaced between said plows, and having means to rotate said impellors at a speed in excess of that of said plows to disperse said resin said longitudinal axis the improvement which comprises means for circulating a heating medium through said jacket, a gas inlet and gas outlet opening at opposite ends of said chamber above the axis thereof, means for forcing low pressure gas through said chamber as said shaft rotates to remove a fines portion of said molding resin from said chamber, means downstream of said chamber to remove the fines portion from the gas and means for controlling the moisture content and temperature of said gas.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,831,290 Dated August 27, 1974

Inventor(s) I. Luis Gomez and Samuel Steingiser

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 14, line 15, after "toward" cancel "", and insert - - - and - - -. Column 14, line 15, after "below" insert - - - said longitudinal axis - - -. Column 14, line 15, after "plows" cancel "",. Column 14, line 16, "impellors" should read - - - impellers - - -. Column 14, lines 16 and 17, cancel "said longitudinal axis" and insert - - - , - - -.

Signed and sealed this 26th day of November 1974.

(SEAL)
Attest:

McCoy M. Gibson Jr. C. Marshall Dann
Attesting Officer Commissioner of Patents