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METHOD FOR PREPARING BROMINATED ISOOLEFIN-POLYOLEFIN INTERPOLYMER DERIVATIVES

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This invention relates to a novel improvement in the method of making brominated isoolefin-polyolefin interpolymer derivatives and relates more specifically to bromination of isoolefin-polyolefin interpolymers with bromohydantoins.

U. S. Patent 2,631,984 describes brominated isoolefin-polyolefin interpolymers and methods for their preparation. Among the methods therein described appears a "dry process" wherein a solid brominating agent such as N-bromoacetamide is mixed with the appropriate interpolymer on a mixing mill and heated to obtain the interpolymer derivative. Although successful in preparing the desired brominated derivative, this method has been found to be very disadvantageous as a result of scoring or corrosion of the mixing mill roll surfaces to such an extent that the process cannot be used on a commercial scale. Further, high temperatures and extended periods of heating time are required to fully develop the brominated derivative which aggregates the corrosion of the mill roll surfaces when the heating is done on the mills.

It is accordingly among the objects of this invention to provide a "dry process" method of bromination which may be effected in standard rubber mixing equipment such as mills, internal mixers and the like, which process does not cause corrosion of areas exposed to and in contact with the interpolymer-brominating agent mixture. It is also an object of this invention to provide a novel class of brominating agents for preparing brominated isoolefin-polyolefin interpolymer derivatives. Another object is to provide an improved process whereby the brominated interpolymer derivative is developed in a shorter period of time at lower temperatures than is possible with such brominating agents as N-bromoacetamide. Other objects will be apparent from the description of the invention that follows.

It now has been discovered that the above-listed objects are achieved by the use of a bromohydantoin for the "dry process" bromination of isoolefin-polyolefin interploymers. The improvement in the "dry process" comprises adding a bromohydantoin to the desired isoolefin-polyolefin interpolymer on a mill or in an internal mixer, intimately mixing the two and thereafter heating the resultant composition in apparatus other than the mixing apparatus so that the interpolymer derivative is developed after the initial mixing operation. The bromohydantoins have been found to be unique among solid brominating agents in ease and uniformity of dispersion and in not causing corrosion of mixing equipment surfaces when mixed with the appropriate isoolefin-polyolefin interpolymer at the normal mixing temperatures of about 100° F. to 135° F. or even higher. When N-bromoacetamide or N-bromosuccinimide is mixed on a mill with Butyl rubber at this nomal temperature of mixing, or even at lower temperatures, the mill roll surfaces are corroded even after very short exposure times and even when the mill rolls are kept cool by suitable cooling means. A further unexpected advantage accruing from the use of bromohydantoins as solid brominating agents for isoolefin-polyolefin interpolymers is the rapid rate at which the brominated interpolymer derivative is developed at higher temperatures, being faster in this aspect than N-bromoacetamide and thus may be effective at lower temperatures. Since the bromination of the isoolefin-polyolefin interpolymers mixed with bromohydantoins apparently does not occur at the ordinary temperatures of mixing, the compounded mixture may be prepared in a single operation at a temperature below 170° F. and preferably below 150° F., and at some later time the brominated derivative is developed as desired. This improvement is most advantageous on a production scale allowing operations which are more economical and which provide for better production control, planning and utilization of equipment and a more uniform product. For example, the stable mixture of bromohydantoin and interpolymer may be mixed in one operation and stored or supplied as a stable mixture, the brominated derivative to be developed as needed or desired. Likewise, a stable masterbatch containing large proportions of the bromohydantoin in interpolymer may be prepared and stored until required and then more efficiently mixed with a sufficient quantity of interpolymer so as to obtain a final product of the desired bromine content after heating. When the usual solid brominating agents are so employed, bromination of the interpolymer begins on the mill and apparently continues during the storage period resulting in degradation of the product.

Quite unexpectedly it has been found that the bromination process with bromohydantoin may be effected in the presence of carbon black. This is most advantageous since difficulty is experienced in obtaining sheets of the bromohydantoin-interpolymer mixture of uniform thickness. When the sheets are not of uniform thickness, the thin portions of the sheet receive too much heat and the thicker portions are not efficiently heated and a uniform derivative having reproducible properties is not obtained. This problem is alleviated when carbon black is employed. Amounts of carbon black varying from about 5 to 100 weight parts are employed with amounts from about 10 to 50 preferably employed. Any of the carbon blacks are useful including the so-called furnace and channel blacks and the like. When large amounts of carbon black are present in the mixture, it may be desirable to increase the amount of bromohydantoin up to about 25 percent of that normally employed. A finely-divided silicon oxide such as any of the fumed, arc or combustion silicon oxides and dried finely-divided silica gel precipitates and the like may be used in place of part or all of the carbon black. Finely-divided silicon dioxide and mixtures of silicon and silicon dioxide are preferred.

During the heating step, the bromine atoms of the brominating agent are introduced into the polymer structure of the isoolefin-polyolefin interpolymer which results in the obtainment of new materials with properties unexpectedly superior to those of the bromine-free interpolymers. These brominated rubbery isoolefin-polyolefin interpolymers cure or vulcanize quite rapidly even with vulcanizing agents, which are totally ineffective with the unbrominated materials, to yield vulcanized products which far surpass those obtained from the unbrominated materials. In addition the brominated interpolymers, unlike the unbrominated materials, adhere well to a wide variety of materials including natural and synthetic rubber and are of value as adhesives. The bromine-containing interpolymers also may be mixed with natural rubber or any of the various synthetic rubbers in any desired proportions, and the resulting mixtures covulcanized to give products of excellent properties.

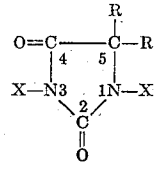
In the practice of the improved process of this invention, an amount of an N-bromohydantoin sufficient to give the desired bromine content in any selected isoolefin-

polyolefin interpolymer is intimately mixed with the interpolymer, for example, on a cold mill or in an internal mixer, and thereafter the mixture is heated to develop the brominated interpolymer derivative. The improved process of this invention is applied to any of those isoolefin-polyolefin interpolymers described in U. S. Patent 2,631,984. Among these are, for example, the interpolymers of a major proportion of, desirably, from 70 to 99 weight percent of an isoolefin generally containing from 4 to 8 carbon atoms, such as most desirably, isobutylene or alternatively 3-methyl butene-1, 4-methyl pentene-1, 2-ethyl butene-1, 4-ethyl pentene-1 or the like, or a mixture of such olefins with a minor proportion, desirably, from 1 to 30 weight percent of a polyolefinic hydrocarbon generally containing from 4 to 18 carbon atoms, or two, three or more such hydrocarbons including the following:

(1) acyclic or open-chain conjugated diolefins such as butadiene-1,3 hydrocarbons such as isoprene and the like;
(2) acyclic non-conjugated diolefins such as dimethallyl and its homologs;
(3) Alicyclic diolefins, both conjugated and non-conjugated, such as cyclopentadiene;
(4) Acyclic triolefins;
(5) Alicyclic triolefins such as fulvene;
(6) higher polyolefins such as tetraolefins and the like.

It is to be understood that in addition to the preferred materials set forth above, any of the other known isoolefin-polyolefin interpolymers also may be utilized in this improved process to prepare brominated derivatives; for example, resinous interpolymers of low molecular weight and/or not readily vulcanizable with sulfur, yield, in accordance with this invention, useful brominated derivatives. Similarly, isoolefin-polyolefin interpolymers containing other interpolymerized monomers such as styrene, chlorostyrenes, alkyl styrenes, acrylyl chloride, methallyl chloride and other monoolefinic monomers also are advantageously used to prepare brominated derivatives.

Any of the N-bromohydantoins may be used in the process of this invention. These N-bromohydantoins are represented by the formula



wherein the R's are hydrogen and alkyl radicals and X is hydrogen and bromine. Preferred are mono- and dibromo(1,3-bromo)-alkyl hydantoins wherein R is hydrogen or alkyl radicals containing from 1 to 8 carbon atoms, and at least one R is alkyl. Particularly preferred is 1,3-dibromo-5,5-dimethyl hyantoin. Also useful are N-bromo-5,5-dimethyl hydantoin, N-bromo-5-methyl-5-ethyl hydantoin, 1,3-dibromo-5-methyl-5-ethyl hydantoin, 1,3-dibromohyantoin, 1,3-dibromo-5-methyl-5-isobutyl hydantoin and the like. For economic and other reasons, low molecular weight dibromohydantoins are preferred.

It has been found that the bromination reaction occurs quite readily upon heating the interpolymer-bromohydantoin mixture.

The amount of bromine which reacts with the interpolymer during the heating step depends upon the amount of bromohydantoin present and to a lesser extent upon the time and temperature of heating. Other factors being equal, there appears to be an approximate straight-line relationship between the original concentration of available bromine and the amount of bromine present in the brominated interpolymer. This is quite advantageous since the bromine content of the brominated interpolymer derivatives can be controlled quite closely by regulating the concentration of the brominating agent.

The brominated interpolymer derivatives resulting from the heating step may contain from as little as 0.5 weight percent or 1 to 4, 8, 10 or 20 weight percent or even as much as 50 weight percent of combined bromine, depending on the degree of unsaturation, which in turn depends upon the proportion of polyolefin in the interpolymer. Preferably, the percentage of combined bromine is less than that which would theoretically be present if all the olefinic double bonds (>C=C<) units were completely brominated and still more preferably, for high molecular weight rubbery isoolefin-polyolefin interpolymers containing iodine numbers less than 50 of the nature of Butyl rubber, the percentage of combined bromine is from 20 to 80 percent of the amount which would be present if all the olefinic double bonds were completely brominated. Still more preferably the percentage of combined bromine in such interpolymers is in the range of 1 to 8 percent, and for adhesive applications is in the range of 1.5 to 4 percent. From the foregoing it is apparent that the preferred brominated interpolymers prepared by the process of this invention are not completely saturated, but that they are less unsaturated than the parent unbrominated interpolymers. Their molecular weights are of the same order as the parent unbrominated interpolymer, but are generally somewhat higher because of the presence of the relatively heavy bromine atoms.

As is apparent from the foregoing discussion, the amount of bromohydantoin employed in the process of this invention will depend upon the degree of bromination desired in the interpolymer derivative, and since the bromohydantoins readily give up their bromine atoms when heated, the amount employed can be calculated readily by those skilled in the art. For example, 1,3-dibromo-5,5-dimethyl hydantoin contains about 55.5 weight percent bromine. Therefore, if it is desired to obtain a brominated interpolymer derivative containing about 0.75 weight percent bromine, 1.50 weight percent bromine or 3.0 weight percent bromine, then about 1.35 parts, 2.70 parts or 5.40 parts respectively of 1,3-dibromo-5,5-dimethyl hydantoin are employed. Similarly 1-bromo-5,5-dimethyl hydantoin contains about 38.6 percent bromine, and if an interpolymer derivative containing 3 percent bromine is desired, about 8 parts of the monobromohydantoin are employed.

The time and temperature required to develop the brominated interpolymer derivative from the isoolefin-polyolefin interpolymer-bromohydantoin mixture are interrelated and can be varied as will be obvious to the man skilled in the art. The temperature must be over 170° F. and may be as high as 300° F. or higher for short periods of exposure. It has been found that a polymer of lighter color and with less apparent degradation is prepared by developing the brominated derivative at as low a temperature as possible. Optimum heating times and temperature for thin stocks, about ⅛ inch thick, of the mixture of interpolymer and 1,3 dibromo-5,5-dimethyl hydantoin in an oven, is about 60 to 30 minutes at about 210 to about 235° F. By optimum is meant a product having maximum improved properties by bromination obtained at this time and temperature. For example, a preferred material is prepared by heating a mixture of 6 parts of 1,3-dibromo-5,5-dimethyl hydantoin and the interpolymer at 212° F. for 60 minutes or for 30 minutes at 235° F.

There may be considerable variation in the time and temperature for heating the interpolymer bromohydantoin mixtures and useful products may be obtained under a variety of conditions. As stated above, it has been found that a temperature greater than about 170° F. is necessary to develop a brominated product. Useful products are prepared, for example, at 212° F. by heating for 20, 30, 60, 90 and even 120 minutes, and also by heating, for example, at 280° F. for 5, 10, 20 and even 40 minutes. While the optimum product is developed at the desired lower temperature, useful products also are obtained when

the products are developed in shorter times at higher temperatures, as for example, at temperatures over 300° F. for periods of time less than 5 minutes. Ordinarily heating times of about 120 minutes or less at temperatures of from about 200° F. to about 300° F. produce useful products. It is desired that a combination of lowest temperature and shortest heating time is employed. Ordinarily this will be about 20 to 90 minutes at about 200° F. to about 250° F. with longer times required for thick stocks and shorter times at higher temperatures. Closer control, of course, must be had over mixtures heated for short periods of time at temperatures over 300° F., and processes conducted at lower temperatures are more flexible and result in more uniform products. Operations over 300° F., 350° F., on a continuous basis, where the stock is rapidly heated for short exposure times, are particularly valuable when the mixture is a bromohydantoin and the appropriate interpolymer.

It is to be understood that the brominated derivative may be developed in the mixing apparatus by heating after mixing, if desired, but is preferably done as a separate step.

The practice of the invention and certain preferred embodiments are given in the examples which follow, which also illustrate the advantages of the improved process of the invention. All parts are parts by weight unless otherwise so indicated.

Example I

100 parts of an isobutylene-isoprene copolymer containing about 97.5 percent isobutylene copolymerized with about 2.5 percent isoprene (standard Butyl or GR–I rubber) is placed on a two-roll rubber mill and worked until a uniform sheet appears on one roll. 5.4 parts of 1,3-dibromo-5,5-dimethyl hydantoin are then added to the rolling bank and the brominating agent thoroughly worked into the interpolymer. During the mixing period, cooling water is passed through the mill rolls to keep the compounded mixture cool. Normally the compound while being mixed will have a temperature of about 110 to 125° F. even with cooling. After mixing, the stock is removed from the mill. There is no apparent attack of the mill rolls by the brominating agent evidenced either by discoloration or other corrosion effects. This is to be compared to mixing an equivalent amount of N-bromoacetamide in more of the same interpolymer under the same conditions. In this case, when the stock is taken off the mill, mill corrosion evidenced by a brown rust-like discoloration of the mill rolls is apparent. If such mixing is continued with N-bromoacetamide, the mill rolls become badly corroded, pitted and scored. As seen, this is not the case when a bromohydantoin is used as the brominating agent.

Examples II through IV

To illustrate the valuable products produced by the process of the invention, brominated derivatives are prepared following the procedure outlined in Example I; varying amounts of 1,3-dibromo-5,5-dimethyl hydantoin are milled into the interpolymer of Example I which is then placed in an oven at about 280° F. for 10 minutes to develop the brominated interpolymer derivative. Portions of each of the resulting brominated interpolymer are then compounded in the following recipe and cured at 307° F. for the indicated time.

Material	Parts
Brominated interpolymer	100.0
Carbon black	50.0
Zinc oxide	5.0
Stearic acid	3.0
Mercaptobenzothiazole	0.5
Tetramethyl thiuram disulfide	1.5
Sulfur	2.0

Example II

1.35 PARTS 1,3-DIBROMO-5,5-DIMETHYL HYDANTOIN (0.75 PERCENT BROMINE IN INTERPOLYMER)

Time, Minutes	300% Modulus, p. s. i.	Tensile Strength, p. s. i.	Elongation, Percent
10	280	2,480	840
20	500	2,820	775
30	500	2,700	725
45	650	2,800	650
75	880	2,800	600
90	880	2,800	560

Example III

2.70 PARTS 1,3-DIBROMO-5,5-DIMETHYL HYDANTOIN (1.50 PERCENT BROMINE IN INTERPOLYMER)

Time, Minutes	300% Modulus, p. s. i.	Tensile Strength, p. s. i.	Elongation, percent
10	300	2,280	840
20	350	2,320	800
30	450	2,600	750
45	450	2,350	700
75	550	2,750	715
90	650	2,800	625

Example IV

5.40 PARTS 1,3-DIBROMO-5,5-DIMETHYL HYDANTOIN (3.0 PERCENT BROMINE IN INTERPOLYMER)

Time, Minutes	300% Modulus, p. s. i.	Tensile Strength, p. s. i.	Elongation, percent
10	800	2,620	650
20	720	2,550	600
30	720	2,550	650
45	720	2,580	600
75	500	2,580	600
90	720	2,600	625

Useful products are obtained with a wide range of concentration of bromohydantoins when the improved process of this invention is employed. When these examples are repeated with other N-bromo-dialkyl hydantoins such as 1,3-dibromo-5-methyl-5-isobutyl hydantoin, equally outstanding results are obtained.

Examples V and VI

To illustrate use of the process at lower temperatures, 100 parts of a copolymer of 97.5 percent isobutylene and 2.5 percent isoprene are intimately mixed with 4, 6, 8 and 10 parts of 1,3-dibromo-5,5-dimethyl hydantoin in a mixer at about 100 to 125° F., and later the mixture is heated in an oven for 60 minutes at 212° F. Portions of the products prepared with 6 and 10 parts bromohydantoin are compounded in the following recipe and vulcanized at 307° F.

Material	Parts
Brominated interpolymer	70.0
Natural rubber	30.0
Epoxidized fatty acid ester	1.4
Heptylated diphenylamines	1.0
Carbon black	35.0
Zinc oxide	5.0
Processing oil	10.0
Stearic acid	1.5
Di-orthotolyl guanidine	0.1
Benzothiazyl disulfide	1.0
Sulfur	2.0

The following stress-strain results are obtained on the vulcanizates of the brominated derivatives made with 6 and 10 parts of bromohydantoin.

Example V

6 PARTS BROMOHYDANTOIN

Time, Minutes	300% Modulus, p. s. i.	Tensile Strength, p. s. i.	Elongation, percent
5	300	685	625
10	820	2,025	595
30	960	2,135	525
45	1,050	2,090	495

Example VI

10 PARTS BROMOHYDANTOIN

Time, Minutes	300% Modulus, p. s. i.	Tensile Strength, p. s. i.	Elongation, percent
5	320	790	620
10	775	1,825	530
30	1,075	1,750	435
45	1,135	1,775	415

This process, heating at lower temperatures, also may be employed with other proportions such as 4 and 8 parts of bromohydantoin and at temperatures as low as 200° F., or for 20 to 30 minutes at 235° F. or shorter periods of time at higher temperatures resulting in useful products equivalent to those described above.

Example VII

To illustrate use of a monobromohydantoin in the process of the invention, a brominated derivative is prepared by the process of Example I with 10 parts of N-bromo-dimethyl hydantoin. 70 parts of the derivative is then compounded with natural rubber in the following recipe and the mixture cured at 307° F. for the indicated time.

Material	Parts
Brominated interpolymer	70.0
Natural rubber	30.0
Epoxidized fatty acid ester	1.4
Heptylated diphenylamines	1.0
Carbon black	35.0
Zinc oxide	5.0
Processing oil	10.0
Stearic acid	1.5
Mercaptobenzothiazyl sulfide	1.0
Di-orthotolyl guanidine	0.1
Sulfur	2.0

Time, Minutes	300% Modulus, p. s. i.	Tensile Strength, p. s. i.	Elongation, percent
10	575	1,650	575
20	800	2,025	800
30	850	2,100	850
45	875	1,975	875
75	800	1,815	800

These data show that a useful brominated interpolymer derivative is prepared by the process of this invention from a monobromohydantoin as well as from dibromohydantoins.

Example VIII

To illustrate the advantages of the stable mixture of bromohydantoin and interpolymer, a masterbatch of 42 parts of N-bromoacetamide is mixed on a mill with 58 parts of an interpolymer containing 97.5 percent of isobutylene and 2.5 percent of isoprene at 100° F., the stock being at about 135° F. During the mixing period the mill rolls are badly corroded, small pits appearing in the rolls, and the rolls are discolored. A similar mixing of 1,3-dibromo-5,5-dimethyl hydantoin does not corrode the mill roll surfaces. The mixed stocks are placed in polyethylene bags and allowed to age for two weeks in the dark. After this time the masterbatches are mixed with sufficient interpolymer to result in a product having about 3 percent bound bromine content and heated to develop the brominated derivative. The derivatives are compounded in recipes similar to those given above, and it is found that the N-bromoacetamide masterbatch suffers a loss of greater than 10 percent in tensile strength even over this short storage period, and that the equivalent bromohydantoin material is not similarly degraded by the aging period. It is assumed that the N-bromoacetamide masterbatch is brominated to some extent during the storage period and in the absence of stabilizer, which is added only after the brominated derivative is developed, that the polymer deteriorates, contributing to an over-all decrease in the physical properties of the final product.

Example IX

100 parts of an interpolymer of 97.5 percent isobutylene and 2.5 percent of isoprene are placed on a rubber mill at about 100° F. and adding thereto 15 parts of an easy-processing carbon black and 8 parts of 1,3-dibromo-5,5-dimethyl hydantoin and intimately mixing. A smooth, stable sheet of stock of uniform thickness is thereby obtained which may be stored and which on heating results in a uniform, reproducible brominated derivative having outstanding physical properties. This process may be repeated in an internal mixer, with other quantities of carbon black, other types of carbon blacks, other amounts and types of bromohydantoins and other interpolymers as described hereinbefore with the same outstanding results.

From the foregoing description of the invention it will be seen that the improved process for making brominated isoolefin-polyolefin interpolymer derivatives is a very useful and valuable process. It is apparent that various embodiments and modifications of the invention, in addition to those specifically disclosed and illustrated by examples, may be employed without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. In the dry process for brominating solid, plastic, isoolefin-polyolefin interpolymers, the improvement which comprises intimately mixing an amount of an N-bromohydantoin sufficient to brominate the isoolefin-polyolefin interpolymer to contain at least 0.5 weight percent combined bromine with an interpolymer of 70 to 99 weight percent of an isoolefinic hydrocarbon containing 4 to 8 carbon atoms and a terminal methylene group and 1 to 30 weight percent of a polyolefinic hydrocarbon containing from 4 to 18 carbon atoms at a temperature less than about 170° F. and heating the mixture at a temperature above about 170° F. for a time sufficient to develop the bromine-containing interpolymer derivative.

2. In the dry process for brominating solid, plastic, isoolefin-polyolefin interpolymers, the improvement which comprises intimately mixing at a temperature below 170° F. an amount of an N,N'-dibromohydantoin sufficient to brominate from 20 to 80 percent of the double bonds of the original interpolymer with an interpolymer of 90 to 99 weight percent of an isoolefinic hydrocarbon containing 4 to 8 carbon atoms and a terminal methylene group and 1 to 10 weight percent of a polyolefinic hydrocarbon containing from 4 to 18 carbon atoms and heating the mixture for a time and at a temperature at least equivalent to heating for about 30 to about 90 minutes at about 212° F. whereby the bromine-containing interpolymer derivative is developed.

3. In the dry process for brominating solid, plastic isoolefin-polyolefin interpolymers, the improvement which comprises intimately mixing an amount of an N,N'-dibromoalkyl hydantoin sufficient to brominate the isoolefin-polyolefin interpolymer to contain from 1 to 8 weight percent combined bromine with an interpolymer of 90 to 99 weight percent of isobutylene and 1 to 10 weight percent of a butadiene-1,3 hydrocarbon at a temperature be-

low 170° F. and heating the mixture for a time and temperature at least equivalent to heating for about 60 minutes at about 212° F. whereby the bromine-containing interpolymer derivative is developed.

4. In the dry process for brominating a solid, plastic, rubbery interpolymer of from 99 to 90 weight percent isobutylene and from 10 to 1 weight percent isoprene, the improvement which comprises first intimately mixing from about 2 to 10 weight parts of a 1,3-dibromo-5,5-dialkyl hydantoin with the isoolefin-polyolefin interpolymer at a temperature below 170° F. and thereafter heating the mixture at a temperature of from about 200° F. to about 300° F. for about from 120 to about 5 minutes whereby the bromine-containing interpolymer derivative is developed.

5. In the dry process for preparing a partially-brominated derivative of a rubbery interpolymer of 90 to 99 weight percent isobutylene and 1 to 10 weight percent isoprene, the improvement which comprises first intimately mixing about 2 to 10 weight parts of 1,3-dibromo-5,5-dimethyl hydantoin with the solid interpolymer at a temperature below 170° F. and thereafter heating the mixture at a time and temperature equivalent to heating for about 30 minutes at about 235° F. whereby the bromine-containing interpolymer derivative is developed.

6. In the dry process for preparing a partially-brominated derivative of a rubbery copolymer of about 97.5 percent isobutylene and about 2.5 percent isoprene, the improvement which comprises first intimately mixing about 5 to 8 weight parts of 1,3-dibromo-5,5-dimethyl hydantoin with 100 weight parts of the solid copolymer at a temperature below 150° F. and thereafter heating the mixture at a temperature from 210 to 250° F. for a time of about 60 to 20 minutes whereby the bromine-containing interpolymer derivative is developed.

7. In the dry process for brominating solid, plastic, isoolefin-polyolefin interpolymers, the improvement which comprises intimately mixing carbon black and an amount of an N-bromohydantoin sufficient to brominate the isoolefin-polyolefin interpolymer to contain at least 0.5 weight percent combined bromine with an interpolymer of 90 to 99 weight percent of an isoolefinic hydrocarbon containing 4 to 8 carbon atoms and a terminal methylene group and 1 to 10 weight percent of a polyolefinic hydrocarbon containing from 4 to 18 carbon atoms at a temperature of less than 170° F. and heating the mixture at a temperature above about 170° F. for a time sufficient to develop the bromine-containing interpolymer derivative.

8. In the dry process for brominating solid, plastic, isoolefin-polyolefin interpolymers, the improvement which comprises intimately mixing from about 5 to 100 weight parts of carbon black with the interpolymer and mixing therewith at a temperature of less than about 170° F. an amount of an N,N'-dibromoalkyl hydantoin sufficient to brominate the interpolymer to contain from about 1 to 8 weight percent combined bromine, said interpolymer comprised of 90 to 99 weight percent of isobutylene and 1 to 10 weight percent of a butadiene-1,3 hydrocarbon, and heating the mixture for a time and temperature at least equivalent to heating for about 30 to about 90 minutes at about 212° F. whereby the bromine-containing interpolymer derivative is developed.

9. In the dry process for preparing a partially-brominated derivative of a rubbery interpolymer of 90 to 99 weight percent isobutylene and 1 to 10 weight percent isoprene, the improvement which comprises first intimately mixing about 10 to 50 weight parts of carbon black with the solid interpolymer and then mixing about 2 to 10 weight parts of 1,3-dibromo-5,5-dimethyl hydantoin therewith at a temperature below 170° F. and thereafter heating the mixture for a time and at a temperature equivalent to heating for about 30 minutes at about 235° F. whereby the bromine-containing interpolymer derivative is developed.

10. In the dry process for brominating solid, plastic, isoolefin-polyolefin interpolymers, the improvement which comprises intimately mixing a material selected from the group consisting of a finely-divided silicon oxide and carbon black and an amount of an N-bromohydantoin sufficient to brominate the solid isoolefin-polyolefin interpolymer to contain at least 0.5 weight percent combined bromine of addition with an interpolymer of an isoolefinic hydrocarbon containing 4 to 8 carbon atoms and a terminal methylene group and a polyolefinic hydrocarbon at a temperature of less than 170° F. and thereafter heating the mixture at a temperature above about 170° F. for a time sufficient to develop the bromine-containing interpolymer derivative.

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