



(22) Date de dépôt/Filing Date: 2001/11/27

(41) Mise à la disp. pub./Open to Public Insp.: 2003/05/27

(51) Cl.Int.⁷/Int.Cl.⁷ C08K 5/36, C08K 5/17

(71) Demandeur/Applicant:
BAYER INC., CA

(72) Inventeurs/Inventors:
RESENDES, RUI, CA;
HOPKINS, WILLIAM, CA

(74) Agent: SMART & BIGGAR

(54) Titre : COMPOSES BUTYLIQUES ELASTOMERES AVEC MATIERE DE CHARGE, AYANT UNE MEILLEURE
RESISTANCE AU GRILLAGE

(54) Title: FILLED ELASTOMERIC BUTYL COMPOUNDS WITH IMPROVED SCORCH SAFETY

(57) **Abrégé/Abstract:**

The invention provides a process for preparing a filled halobutyl elastomer, which comprises mixing a halobutyl elastomer, particles of filler an additive containing both amino and alcohol functional groups, and one or more hydrated metal halogenides and optional curing the filled elastomer with sulfur or other curative systems. Those compositions have improved properties when compared to known carbon black-filled halobutyl elastomeric compositions combined with an enhanced scorch safety. This invention has the advantages of (a) not evolving alcohol either during the manufacture or subsequent use of the article manufactured from the compound, and (b) maintaining good processability of the compound.

Filled Elastomeric Butyl Compounds with improved scorch safety

5

ABSTRACT

The invention provides a process for preparing a filled halobutyl elastomer, which comprises mixing a halobutyl elastomer, particles of filler an additive
10 containing both amino and alcohol functional groups, and one or more hydrated metal halogenides and optional curing the filled elastomer with sulfur or other curative systems. Those compositions have improved properties when compared to known carbon black-filled halobutyl elastomeric compositions combined with an enhanced scorch safety. This invention has
15 the advantages of (a) not evolving alcohol either during the manufacture or subsequent use of the article manufactured from the compound, and (b) maintaining good processability of the compound.

Filled Elastomeric Butyl Compounds with improved scorch safety

Field of the Invention

5

The present invention relates to halogenated butyl elastomers with improved scorch safety, in particular bromobutyl elastomers with improved scorch safety.

Background of the invention:

It is known that reinforcing fillers such as carbon black and silica greatly improve the strength and fatigue properties of elastomeric compounds. It is also known that chemical interaction occurs between the elastomer and the filler. For example, good interaction between carbon black and highly unsaturated elastomers such as polybutadiene (BR) and styrene butadiene copolymers (SBR) occurs because of the large number of carbon-carbon double bonds present in these copolymers. Butyl elastomers may have only one tenth, or fewer, of the carbon-carbon double bonds found in BR or SBR, and compounds made from butyl elastomers are known to interact poorly with carbon black. For example, a compound prepared by mixing carbon black with a combination of BR and butyl elastomers results in domains of BR, which contain most of the carbon black, and butyl domains which contain very little carbon black. It is also known that butyl compounds have poor abrasion resistance.

Canadian Patent Application 2,293,149 shows that it is possible to produce filled butyl elastomer compositions with much improved properties by combining halobutyl elastomers with silica and specific silanes. These silanes act as dispersing and bonding agents between the halogenated butyl elastomer and the filler. However, one disadvantage of the use of silanes is the evolution of alcohol during the process of manufacture and potentially during the use of the manufactured article produced by this process.

Additionally, silanes significantly increase the cost of the resulting manufactured article.

Co-pending application CA 2,339,080 discloses a process for preparing compositions containing halobutyl elastomers and organic compounds containing at least one basic nitrogen-containing group and at least one hydroxyl group in which there is enhanced interaction between the elastomer and a filler, especially a mineral filler. Of particular interest were compounds containing primary amine and hydroxyl groups such as ethanolamine. While solving the problem of enhancing the interaction between elastomer and filler, said compositions have to be processed carefully to prevent any undesirable scorch of the composition. The skilled in the art understands the term scorch as premature crosslinking of the composition during processing.

Summary of the Invention:

The present invention provides a process for preparing compositions containing halobutyl elastomers, organic compounds containing at least one basic nitrogen-containing group and at least one hydroxyl group, and hydrated metal halogenides. In this process there is enhanced interaction between the elastomer and a filler, especially a mineral filler with improved scorch safety. The invention also provides filled halobutyl elastomer compositions containing halobutyl elastomers, organic compounds containing at least one basic nitrogen-containing group and at least one hydroxyl group, and one or more hydrated metal halogenides. Those compositions have improved properties when compared to known carbon black-filled halobutyl elastomeric compositions combined with an enhanced scorch safety. In particular it provides a means to produce such filled compositions without the evolution of alcohol.

30

Of particular interest are organic compounds containing at least one basic nitrogen-containing group and at least one hydroxyl group containing primary amine and hydroxyl groups such as ethanolamine. These organic

compounds are believed to disperse and bond the silica to the halogenated elastomers.

Accordingly, in a further aspect the present invention provides a process which comprises mixing a halobutyl elastomer with a filler, especially a mineral filler, in the presence of an additive which is an organic compound which has at least one hydroxyl group and at least one basic nitrogen-containing group and one or more hydrated metal halogenides, and curing the resulting filled halobutyl elastomer. The resulting composition, having improved scorch safety, forms another aspect of the invention.

The halobutyl elastomer that is admixed with the filler and one or more organic compounds which have at least one hydroxyl group and at least one basic nitrogen-containing group and one or more hydrated metal halogenides may be a mixture with another elastomer or elastomeric compound. The halobutyl elastomer should constitute more than 5% of any such mixture. Preferably the halobutyl elastomer should constitute at least 10% of any such mixture. In some cases it is preferred not to use mixtures but to use the halobutyl elastomer as the sole elastomer. If mixtures are to be used, however, then the other elastomer may be, for example, natural rubber, polybutadiene, styrene-butadiene or poly-chloroprene or an elastomer compound containing one or more of these elastomers.

The filled halobutyl elastomer can be cured to obtain a product, which has improved properties, for instance in abrasion resistance, rolling resistance and traction. Curing can be effected with sulfur. The preferred amount of sulfur is from 0.3 to 2.0 parts by weight per hundred parts of rubber. An activator, for example zinc oxide, may also be used, in an amount of from 5 parts to 2 parts by weight. Other ingredients, for instance stearic acid, antioxidants, or accelerators may also be added to the elastomer prior to curing. Sulphur curing is then effected in known manner. See, for instance, chapter 2, "The Compounding and Vulcanization of Rubber", of "Rubber Technology", 3rd edition, published by Chapman & Hall, 1995, the disclosure of which is incorporated by reference.

Other curatives known to cure halobutyl elastomers may also be used. A number of compounds are known to cure BIIIR, for example, such as bis dieneophiles (for example HVA2 = m-phenylene-bis-maleimide) phenolic
5 resins, amines, amino-acids, peroxides, zinc oxide and the like. Combinations of the aforementioned curatives may also be used.

The mineral-filled halobutyl elastomer of the invention can be admixed with other elastomers or elastomeric compounds before it is subjected to the
10 curing with sulphur. This is discussed further below.

Detailed Description of the Invention

The phrase "halobutyl elastomer(s)" as used herein refers to a
15 chlorinated or brominated butyl elastomer. Brominated butyl elastomers are preferred, and the invention is illustrated, by way of example, with reference to such bromobutyl elastomers. It should be understood, however, that the invention extends to the use of chlorinated butyl elastomers.

20 Thus, halobutyl elastomers suitable for use in the practice of this invention include, but are not limited to, brominated butyl elastomers. Such elastomers may be obtained by bromination of butyl rubber (which is a copolymer of isobutylene and a co-monomer that is usually a C₄ to C₆ conjugated diolefin, preferably isoprene). Co-monomers other than
25 conjugated diolefins can be used, however, and mention is made of alkyl-substituted vinyl aromatic co-monomers such as C₁-C₄-alkyl substituted styrene. An example of such an elastomer which is commercially available is brominated isobutylene methylstyrene copolymer (BIMS) in which the co-monomer is p-methylstyrene.

30

Brominated butyl elastomer typically contains from 1 to 3 weight percent of isoprene and from 97 to 99 weight percent of isobutylene (based upon the hydrocarbon content of the polymer) and from 1 to 4 weight percent

bromine (based upon the bromobutyl polymer). A typical bromobutyl polymer has a molecular weight, expressed as the Mooney viscosity (ML 1 + 8 at 125°C), of from 28 to 55.

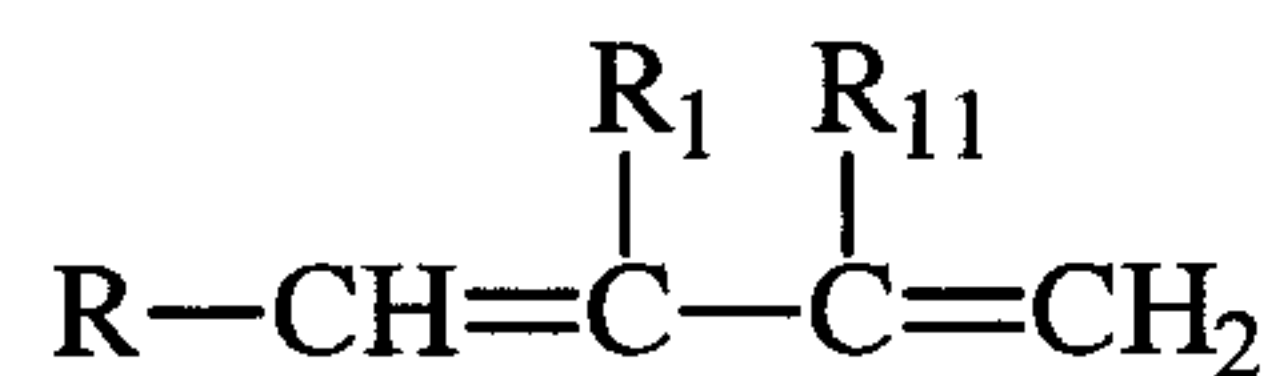
5 For use in the present invention the brominated butyl elastomer preferably contains in the range of from 1 to 5 weight percent of isoprene and from 95 to 99 weight percent of isobutylene (based upon the hydrocarbon content of the polymer) and from 0.5 to 2.5 weight percent, preferably from 0.75 to 2.3 weight percent, of bromine (based upon the brominated butyl
10 polymer).

A stabilizer may be added to the brominated butyl elastomer. Suitable stabilizers include calcium stearate and epoxidized soy bean oil, preferably used in an amount in the range of from 0.5 to 5 parts by weight per 100 parts
15 by weight of the brominated butyl rubber.

Examples of suitable brominated butyl elastomers include Bayer Bromobutyl® 2030, Bayer Bromobutyl® 2040 (BB2040), and Bayer Bromobutyl® X2 commercially available from Bayer Inc. Bayer BB2040 has a
20 Mooney viscosity (RPML 1+8 @ 125°C according to ASTM D 52-89) of 39 ± 4 , a bromine content of 2.0 ± 0.3 wt% and an approximate molecular weight Mw of 500,000 grams per mole.

The brominated butyl elastomer used in the process of this invention
25 may also be a graft copolymer of a brominated butyl rubber and a polymer based upon a conjugated diolefin monomer. Our co-pending Canadian Patent Application 2,279,085 is directed towards a process for preparing such graft copolymers by mixing solid brominated butyl rubber with a solid polymer based on a conjugated diolefin monomer which also includes some C-S-(S)_n-
30 C bonds, where n is an integer from 1 to 7, the mixing being carried out at a temperature greater than 50°C and for a time sufficient to cause grafting. The disclosure of this application is incorporated herein by reference. The bromobutyl elastomer of the graft copolymer can be any of those described

above. The conjugated diolefins that can be incorporated in the graft copolymer generally have the structural formula :



5

wherein R is a hydrogen atom or an alkyl group containing from 1 to 8 carbon atoms and wherein R₁ and R₁₁ can be the same or different and are selected from the group consisting of hydrogen atoms and alkyl groups containing from 1 to 4 carbon atoms. Some representative non-limiting
 10 examples of suitable conjugated diolefins include 1,3-butadiene, isoprene, 2-methyl-1,3-pentadiene, 4-butyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 1,3-hexadiene, 1,3-octadiene, 2,3-dibutyl-1,3-pentadiene, 2-ethyl-1,3-pentadiene, 2-ethyl-1,3-butadiene and the like. Conjugated diolefin monomers containing from 4 to 8 carbon atoms are preferred, 1,3-butadiene
 15 and isoprene being especially preferred.

20

The polymer based on a conjugated diene monomer can be a homopolymer, or a copolymer of two or more conjugated diene monomers, or a copolymer with a vinyl aromatic monomer.

25

30

The vinyl aromatic monomers which can optionally be used are selected so as to be copolymerizable with the conjugated diolefin monomers being employed. Generally, any vinyl aromatic monomer which is known to polymerize with organo-alkali metal initiators can be used. Such vinyl
 aromatic monomers usually contain from 8 to 20 carbon atoms, preferably from 8 to 14 carbon atoms. Some examples of vinyl aromatic monomers which can be so copolymerized include styrene, alpha-methyl styrene, various alkyl styrenes including p-methylstyrene, p-methoxy styrene, 1-vinylnaphthalene, 2-vinyl naphthalene, 4-vinyl toluene and the like. Styrene is
 preferred for copolymerization with 1,3-butadiene alone or for terpolymerization with both 1,3-butadiene and isoprene.

The filler is composed of particles of a mineral, and examples include silica, silicates, clay (such as bentonite), gypsum, alumina, aluminum oxide, magnesium oxide, calcium oxide, titanium dioxide, talc and the like, as well as mixtures thereof. These mineral particles have hydroxyl groups on their surface, rendering them hydrophilic and oleophobic. This exacerbates the difficulty of achieving good interaction between the filler particles and the butyl elastomer. For many purposes, the preferred mineral is silica, especially silica prepared by the carbon dioxide precipitation of sodium silicate.

Dried amorphous silica particles suitable for use in accordance with the invention have a mean agglomerate particle size between 1 and 100 microns, preferably between 10 and 50 microns and most preferably between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, of between 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, of between 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/11, of from 0 to 10 percent by weight. Suitable silica fillers are available under the trademarks HiSil® 210, HiSil® 233 and HiSil 243 from PPG Industries Inc. Also suitable are Vulkasil® S and Vulkasil® N, from Bayer AG.

Carbon black is not normally used as a filler in the halobutyl elastomer compositions of the invention, but in some embodiments it may be present in an amount up to 40 phr. If the mineral filler is silica and it is used with carbon black, the silica should constitute at least 55% by weight of the total of silica and carbon black. If the halobutyl elastomer composition of the invention is blended with another elastomeric composition, that other composition may contain carbon black as a filler.

The amount of filler to be incorporated into the halobutyl elastomer can vary between wide limits. Typical amounts of filler range from 20 parts to 120

parts by weight, preferably from 30 parts to 100 parts, more preferably from 40 to 80 parts per hundred parts of elastomer.

5 The organic compound which has at least one hydroxyl group and at least one basic nitrogen-containing group contains at least one hydroxyl group, which (without being bound to any particular theory) may react with the mineral filler, and at least one group containing a basic nitrogen atom, which (without being similarly bound) may react with the active halogen in a halogenated butyl elastomer (for example with the active bromine atom in a brominated butyl elastomer). Functional groups containing –OH may be, for example, alcohols or carboxylic acids. Functional groups containing a basic nitrogen atom include, but are not limited to, amines (which can be primary, secondary or tertiary) and amides. Preferred are primary alkyl amine groups such as aminoethyl, aminopropyl and the like.

15

Examples of organic compound which has at least one hydroxyl group and at least one basic nitrogen-containing group which give enhanced physical properties to mixtures of halobutyl elastomers and especially silica include proteins, aspartic acid, 6-aminocaproic acid, diethanolamine and triethanolamine. Preferably, the additive should contain a primary alcohol group and a primary amino group separated by methylene bridges, which may be branched. Such compounds have the general formula HO-A-NH₂; wherein A represents a C1 to C20 alkylene group, which may be linear or branched.

25 More preferably, the number of methylene groups between the two functional groups should be between 1 and 4. Examples of preferred additives include mono-ethanolamine and 3-amino-1-propanol.

30 The amount of the organic compound which has at least one hydroxyl group and at least one basic nitrogen-containing group used is dependent upon the molecular/equivalent weight of each specific compound. One important factor is the number/weight of nitrogen per unit weight of the compound. The level of nitrogen may range from 0.1 to 5 parts per hundred (phr) of halobutyl rubber, preferably from 0.125 to 1 phr and, more preferably,

from 0.3 to 0.7 phr. Up to 40 parts of processing oil, preferably from 5 to 20 parts, per hundred parts of elastomer, may be present. Further, a lubricant, for example a fatty acid such as stearic acid, may be present in an amount up to 3 parts by weight, more preferably in an amount up to 2 parts by weight.

5

The hydrated metal halogenide will have the general formula $MX_n(mH_2O)$, in which M denotes for a metal selected from groups 1-16 of the periodic system of the element according to IUPAC 1985, X is selected from the group consisting of fluorine, chlorine, bromine and iodine and mixtures thereof, n is the number of halogenides needed to compensate the positive charge of the metal ion and m is the average number of water molecules which typically surround the positively charged metal ion. The value m is typically determined through X-ray structural analysis or through various gravimetric techniques typically used by those skilled in the art.

15

Preferred metals are selected from the groups 3 to 12 according to IUPAC and include Cr, Ni, Co and Fe.

Preferred halogenides are chlorine and bromine.

20

The metal halogenides are usually added in an amount of from 0.1 to 20 phr, preferably of from 2 to 10.

The metal halogenides are especially useful in improving the scorch safety of compounds comprising primary aminoalcohols.

25

The halobutyl elastomer, filler and additives are mixed together, suitably at a temperature in the range of from 25 to 200°C. It is preferred that the temperature in one of the mixing stages be greater than 60°C, and a temperature in the range of from 90 to 150°C is particularly preferred. Normally the mixing time does not exceed one hour; a time in the range from 2 to 30 minutes is usually adequate. The mixing is suitably carried out on a two-roll mill mixer, which provides good dispersion of the filler within the

30

elastomer. Mixing may also be carried out in a Banbury mixer, or in a Haake or Brabender miniature internal mixer. An extruder also provides good mixing, and has the further advantage that it permits shorter mixing times. It is also possible to carry out the mixing in two or more stages. Further, the
5 mixing can be carried out in different apparatuses, for example one stage may be carried out in an internal mixer and another in an extruder.

The order of addition of the different components to the rubber is not critical, however, it might be advantageous to mix the metal halogenide(s), the
10 filler(s) and the organic compound which has at least one hydroxyl group and at least one basic nitrogen-containing group contains at least one hydroxyl group prior to the addition of the rubber.

The enhanced interaction between the filler and the halobutyl
15 elastomer results in improved properties for the filled elastomer. These improved properties include higher tensile strength, higher abrasion resistance, lower permeability and better dynamic properties. These render the filled elastomers particularly suitable for a number of applications, including, but not limited to, use in tire treads and tire sidewalls, tire
20 innerliners, tank linings, hoses, rollers, conveyor belts, curing bladders, gas masks, pharmaceutical enclosures and gaskets. These advantages are achieved together with an enhancement in scorch safety.

In a preferred embodiment of the invention, bromobutyl elastomer,
25 silica particles, organic compound which has at least one hydroxyl group and at least one basic nitrogen-containing group, one or more of the metal halogenides and, optionally, processing oil extender are mixed on a two-roll mill at a nominal mill temperature of 25°C. The mixed compound is then placed on a two-roll mill and mixed at a temperature above 60°C. It is
30 preferred that the temperature of the mixing is not too high, and more preferably does not exceed 150°C, since higher temperatures may cause curing to proceed undesirably far and thus impede subsequent processing. The product of mixing these ingredients at a temperature not exceeding

150°C is a compound which has good stress/strain properties and which can be readily processed further on a warm mill with the addition of curatives.

5 The filled halobutyl rubber compositions of the invention, and in particular filled bromobutyl rubber compositions, find many uses, but mention is made particularly of use in tire tread compositions. Important features of a tire tread composition are that it shall have low rolling resistance, good traction, particularly in the wet, and good abrasion resistance so that it is resistant to wear. Compositions of the invention display improved resistance
10 to wear when compared to compounds which contain no organic modifier nor hydrated metal halogenide while possessing improved scorch safety. As is demonstrated in the examples below, compositions of the invention display improved resistance to wear with enhanced scorch safety.

15 The filled halobutyl elastomers of this invention can be further mixed with other rubbers, for example natural rubber, butadiene rubber, styrene-butadiene rubber and isoprene rubbers, and compounds contain these elastomers.

20 The invention is further illustrated in the following examples and the accompanying Figures.

Examples:Description of tests:

Abrasion resistance: DIN 53-516 (60 grit Emery paper)

5

Cure rheometry: ASTM D 52-89 MDR2000E Rheometer at 1° arc and 1.7 Hz

RPA analysis. 100 °C at a frequency of 30 cpm at strains of 0.5, 1, 2, 5, 10, 20, 50 and 90 %.

- 10 *Compound Mooney Scorch.* Measurements were conducted at 135 °C using a small rotor. The t03 value obtained with the small rotor is equivalent to the t05 value (large rotor) typically quoted.

- 15 *Stress-strain.* Samples were prepared by curing a macro sheet at 170 °C for tc90+5 minutes, after which the appropriate sample was dyed out. The test was conducted at 23 °C.

Description of Ingredients and General Mixing Procedure:

Hi-Sil® 233 - silica - a product of PPG

- 20 Sunpar® 2280 - paraffinic oil produced by Sun Oil.

Maglite® D – magnesium oxide by C.P.Hall

- 25 The brominated butyl elastomer, silica, oil, bonding compound and hydrated metal halogenide were mixed in a 1.57 liter Banbury internal tangential mixture with the Mokon set to 40 °C and a rotor speed of to 77 RPM. Curatives were then added to the cooled sample with a 6" x 12" mill at 25°C.

Example 1

- 30 The effect of $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ on the degree of reinforcement (as denoted by the M300/M100 values), degree of silica dispersion, DIN abrasion resistance and scorch safety (as denoted by the t03 times in minutes) in compounds containing brominated butyl rubber, HiSil® 233, Maglite® D and ethanolamine

was studied. A compound containing only brominated butyl rubber, HiSil® 233 and Maglite® D was used as a control. All of the compounds studied utilized a mixture of 0.5 phr of sulfur, 1.5 phr of zinc oxide and 1.0 phr of stearic acid as the curative system.

5

The following levels of $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ were studied:

- (i) 0 phr $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$
- (ii) 2.4 phr $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$
- (iii) 4.8 phr $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$
- 10 (iv) 9.7 phr $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$

All compounds, except for the control used 2.2 phr of ethanolamine as the organic additive containing at least one amino group and at least one hydroxyl group.

15

Brominated isoprene isobutylene rubber (BIIR) was mixed with the additive, 60 parts per hundred rubber (phr) of silica filler (HiSil® 233) in a Banbury internal mixer under the mixing conditions described above. Identical curative ingredients (1 phr of stearic acid, 0.5 phr of sulfur, and 1.5phr of ZnO) were
20 then added on a cool mill to each of the compounds. The compounds were then cured for either $t_{c(90)} + 10$ minutes at 170 °C (for DIN Abrasion testing) or $t_{c(90)} + 5$ minutes at 170°C and tested. Table 1 gives the product compositions, and physical property data for the $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ containing compounds and for a compound containing no filler bonding agent.

TABLE 1 Master Batch Mix

Example	1a	1b	1c	1d	1e
<i>Coupling Agent</i>	<i>9.7 phr FeCl₃</i>	<i>4.8 phr FeCl₃</i>	<i>2.4 phr FeCl₃</i>	<i>0 phr FeCl₃</i>	<i>Control</i>
STRESS STRAIN (DUMBELLS)					
Cure Time (min)	25	23	25	19	34
Cure Temperature (°C)	170	170	170	170	170
Dumbell	Die C	Die C	Die C	Die C	Die C
Test Temperature (°C)	23	23	23	23	23
Hard. Shore A2 Inst. (pts.)	74	76	75	72	76
Ultimate Tensile (MPa)	15.04	14.45	14.1	17.53	4.9
Ultimate Elongation (%)	646	671	515	343	746
Strain (% Elongation)	<i>9.7 phr FeCl₃</i>	<i>4.8 phr FeCl₃</i>	<i>2.4 phr FeCl₃</i>	<i>0 phr FeCl₃</i>	<i>Control</i>
25	1.62	1.72	1.78	1.83	1.74
50	1.62	1.65	1.88	2.31	1.57
100	1.9	1.8	2.64	3.67	1.62
200	3.26	2.74	5.48	8.24	1.6
300	4.97	4.15	8.34	14.5	1.81
	Stress (MPa)	Stress (MPa)	Stress (MPa)	Stress (MPa)	Stress (MPa)
300/100	2.62	2.31	3.16	3.95	1.02
DIN ABRASION					
Abrasion Volume Loss (mm³)	347	336	320	255	TSTM
COMPOUND MOONEY SCORCH					
t Value t03 (min)	5.32	2.55	7.47	1.36	>30
MDR CURE CHARACTERISTICS					
MH (dN.m)	32.52	36.43	38.32	41.58	27.05
ML (dN.m)	16.84	18.04	16.72	14.05	19.62
Delta MH-ML (dN.m)	15.68	18.39	21.6	27.53	7.43
ts 1 (min)	1.02	0.96	0.36	0.3	1.5
ts 2 (min)	1.56	1.32	0.54	0.42	3
t' 10 (min)	1.29	1.24	0.54	0.44	1.13
t' 25 (min)	2.66	2.26	1.2	0.92	2.73
t' 50 (min)	6.14	5.29	3.22	2.82	7.23
t' 90 (min)	20.38	18.34	20.94	13.55	28
t' 95 (min)	25.73	22.23	27.42	18.08	33.4
Delta t'50 - t'10 (min)	4.85	4.05	2.68	2.38	6.1
RPA Payne Effect					
Strain	<i>9.7 phr FeCl₃</i>	<i>4.8 phr FeCl₃</i>	<i>2.4 phr FeCl₃</i>	<i>0 phr FeCl₃</i>	<i>Control</i>
0.28	2030.6	2837.8	1807.4		2442.8
0.98	2212.9	3319.8	2024.6	849.29	2518.6
1.95	2137.9	3158.1	2016.1	937.58	2459.2
4.05	1816.3	2465.5	1736.6	950.73	2110.8
7.95	1360.9	1643.4	1302	881.04	1574.8
16.04	877.94	990.26	859.99	718.01	1029.5
31.95	538.56	581.1	534.26	526.43	642.99
64.03	320.77	336.77	317.42	346.68	387.5
124.99	196.69	204.87	192.01	220.23	235.31
249.98	117.02	124.12	116.12	137.73	135.79
450.03	75.745	79.012	78.495	99.171	81.191

The data in Table 1 clearly shows the effect of adding $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ and monoethanolamine to assist in the dispersion and bonding of the filler in the brominated butyl elastomer, especially when compared to the control compound. The ratio M300/M100 is commonly used as a relative measure of the degree of filler reinforcement in an elastomer compound (the higher the ratio the higher the reinforcement). M300 / M100 for the control (no silane or $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$) is 1.02 and for $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ and ethanolamine containing compounds ranges from 2.31 to 3.95. The stress-strain profile shown in Figure 1 further emphasizes this point.

The value of the complex modulus (G^*) at low strain levels is commonly taken as a measure of silica dispersion (the lower the G^* value at low strains, the better the silica dispersion). Figure 2 shows the dependence of this value on the loading of $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$. Importantly, significantly improved silica dispersion is seen for compounds which contain monoethanolamine and $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ as compared the control compound.

Examination of the DIN Abrasion test data show that the incorporation of monoethanolamine and $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ into these compounds significantly improves wear. The control compound was far too soft to be measured (TSTM).

The t03 time obtained from a Mooney Scorch measurement is taken to be representative of the scorch safety possessed by a rubber pre-vulcanizate. As the t03 increases, so does the processability. From the data presented in Table 1, it is clear that the incorporation of mixtures of monoethanolamine and $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ into these compounds improves the scorch safety (lowers the t03 times) when compared to the control compound or to the compound which contains only monoethanolamine. This particular observation illustrates the role of $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ on the scorch safety, and thus processability, of these compounds.

Example 2

The effect of $\text{NiCl}_2 \cdot x\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot x\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot x\text{H}_2\text{O}$ on the degree of reinforcement (as denoted by the M300/M100 values), degree of silica dispersion, DIN abrasion resistance and scorch safety (as denoted by the t03
5 times in minutes) in compounds containing brominated butyl rubber, HiSil® 233, Maglite® D and ethanolamine was studied. A compound containing only brominated butyl rubber, HiSil® 233, monoethanolamine and Maglite® D was used as a control. All of the compounds studied utilized a mixture of 0.5 phr of sulfur, 1.5 phr of zinc oxide and 1.0 phr of stearic acid as the curative
10 system.

The following levels of hydrated metal halogenides were studied:

- (i) 0 phr (Control)
- 15 (ii) 8.5 phr $\text{NiCl}_2 \cdot x\text{H}_2\text{O}$
- (iii) 9.6 phr $\text{CrCl}_3 \cdot x\text{H}_2\text{O}$
- (iv) 8.6 phr $\text{CoCl}_2 \cdot x\text{H}_2\text{O}$

All compounds used 2.2 phr of ethanolamine as the organic additive
20 containing at least one amino group and at least one hydroxyl group.

Brominated isoprene isobutylene rubber (BIIR) was mixed with the additive, 60 parts per hundred (phr) of silica filler (HiSil® 233) in a Banbury internal mixer under the mixing conditions described above. Identical curative
25 ingredients (1 phr of stearic acid, 0.5 phr of sulfur, and 1.5 phr of ZnO) were then added on a cool mill to each of the compounds. The compounds were then cured for either $t_c(90) + 10$ minutes at 170 °C (for DIN Abrasion testing) or $t_c(90) + 5$ minutes at 170 °C and tested. Table 2 gives the product compositions, and physical property data for the hydrated metal halogenide
30 containing compounds and for the control compound which contains only monoethanolamine.

That data in Table 2 clearly shows the effect of adding a hydrated metal halogenide to BIIR/HiSil/monoethanolamine compounds. Importantly, significant differences are seen on varying the metal center. This would indicate, as expected, a dependence on the degree of interaction between the
5 monoethanolamine and the metal center to the nucleophilicity of that metal center.

As the data in Table 2 illustrates, the interaction of the hydrated metal halogenides with the monoethanolamine suppresses the function of the
10 monoethanolamine as a dispersing and linking agent for silica within BIIR. However, it is important to note the improvements in t03 times which are observed when the hydrated metal halogenides are incorporated into the rubber compound (Figure 3).

TABLE 2

Example	2a	2b	2c	2d
<i>Coupling Agent</i>	<i>None</i>	<i>8.5 NiCl₂ (xH₂O)</i>	<i>9.6 CrCl₃ (xH₂O)</i>	<i>8.6 CoCl₂ (xH₂O)</i>
STRESS STRAIN (DUMBELLS)				
Cure Time (min)	19	21	28	21
Cure Temperature (°C)	170	170	170	170
Dumbell	Die C	Die C	Die C	Die C
Test Temperature (°C)	23	23	23	23
Hard. Shore A2 Inst. (pts.)	72	71	62	72
Ultimate Tensile (MPa)	17.53	13.92	12.15	13.48
Ultimate Elongation (%)	343	863	1012	897
Strain (% Elongation)	<i>None</i>	<i>8.5 NiCl₂ (xH₂O)</i>	<i>9.6 CrCl₃ (xH₂O)</i>	<i>8.6 CoCl₂ (xH₂O)</i>
25	1.83	1.51	1.21	1.59
50	2.31	1.45	1.14	1.54
100	3.67	1.53	1.15	1.52
200	8.24	2.2	1.51	1.9
300	14.5	3.39	2.26	2.74
	Stress (MPa)	Stress (MPa)	Stress (MPa)	Stress (MPa)
300/100	3.95	2.22	1.97	1.80
DIN ABRASION				
Abrasion Volume Loss (mm³)	255	345	399	374
COMPOUND MOONEY SCORCH				
t Value t03 (min)	1.36	2.91	26.03	3.15
MDR CURE CHARACTERISTICS				
MH (dN.m)	41.58	29.27	22.58	30.65
ML (dN.m)	14.05	13.67	13.19	14.34
Delta MH-ML (dN.m)	27.53	15.6	9.39	16.31
ts 1 (min)	0.3	1.62	2.58	1.2
ts 2 (min)	0.42	2.4	4.14	1.74
t' 10 (min)	0.44	2.03	2.5	1.51
t' 25 (min)	0.92	3.78	4.82	2.92
t' 50 (min)	2.82	7.13	11.25	6.14
t' 90 (min)	13.55	16.24	32.9	16.2
t' 95 (min)	18.08	18.68	39.24	18.99
Delta t'50 - t'10 (min)	2.38	5.1	8.75	4.63
RPA Payne Effect				
Strain	<i>None</i>	<i>8.5 NiCl₂ (xH₂O)</i>	<i>9.6 CrCl₃ (xH₂O)</i>	<i>8.6 CoCl₂ (xH₂O)</i>
0.98	849.29	1721.4	1518.8	1967.4
1.95	937.58	1840.3	1770.9	2080.3
4.05	950.73	1554.1	1561.1	1692
7.95	881.04	1132.8	1148.8	1189
16.04	718.01	734.77	726.52	752.33
31.95	526.43	457.16	431.18	461.02
64.03	346.68	279.81	243.56	279.01
124.99	220.23	180.07	139.64	178.54
249.98	137.73	116.09	78.85	115.1
450.03	99.171	77.572	49.298	76.902

CLAIMS:

1. A process for preparing a filled halobutyl elastomer which comprises
5 admixing a halobutyl elastomer, particles of filler, an organic compound
which has at least one hydroxyl group and one basic nitrogen-
containing group, and one or more hydrated metal halogenides, and
curing the resulting filled brominated butyl elastomer.
2. A process according to claim 1, wherein the basic nitrogen-containing
10 group is an amino group.
3. A process according to claim 2 wherein the amino group is a primary
amino group.
4. A process according to claim 1, wherein the organic compound which
has at least one hydroxyl group and one basic nitrogen-containing
15 group has an amine group and a carboxylic acid group.
5. A process according to claim 4, wherein the organic compound which
has at least one hydroxyl group and one basic nitrogen-containing
group is an amino acid.
6. A process according to claim 1, wherein the organic compound which
20 has at least one hydroxyl group and one basic nitrogen-containing
group is an aminoalcohol.
7. A process according to claim 1, wherein the metal halogenide is a
metal bromide or chloride.
8. A process according to claim 1, wherein the amount of organic
25 compound which has at least one hydroxyl group and one basic
nitrogen-containing group used results in a nitrogen level in the
elastomer of from 0.1 to 5 parts per hundred parts of elastomer
9. A process according to claim 1, wherein the metal halogenide is used
in an amount of from 0.1 to 10 phr.
- 30 10. A process according to claim 1, wherein the filler is silica or carbon
black.
11. A process according to claim 1 wherein the filled halobutyl elastomer is
admixed with another elastomer or elastomeric compound before it is
subjected to curing.

12. A process according to claim 1, wherein the filled halobutyl elastomer is cured with 0.3 to 2.0 parts by weight of sulfur.
13. A filled, halobutyl elastomer composition comprising at least one halobutyl elastomer, particles of filler, at least one an organic
5 compound which has at least one hydroxyl group and one basic nitrogen-containing group, and one or more hydrated metal halogenides.
14. A filled, cured elastomer composition prepared by a process according to claim 1.
- 10 15. A filled, cured elastomer composition according to claim 14 in the form of a tread for a vehicle tire.
16. A filled, cured elastomer composition according to claim 15 in the form of an innerliner for a vehicle tire.

15

FIGURE 1.

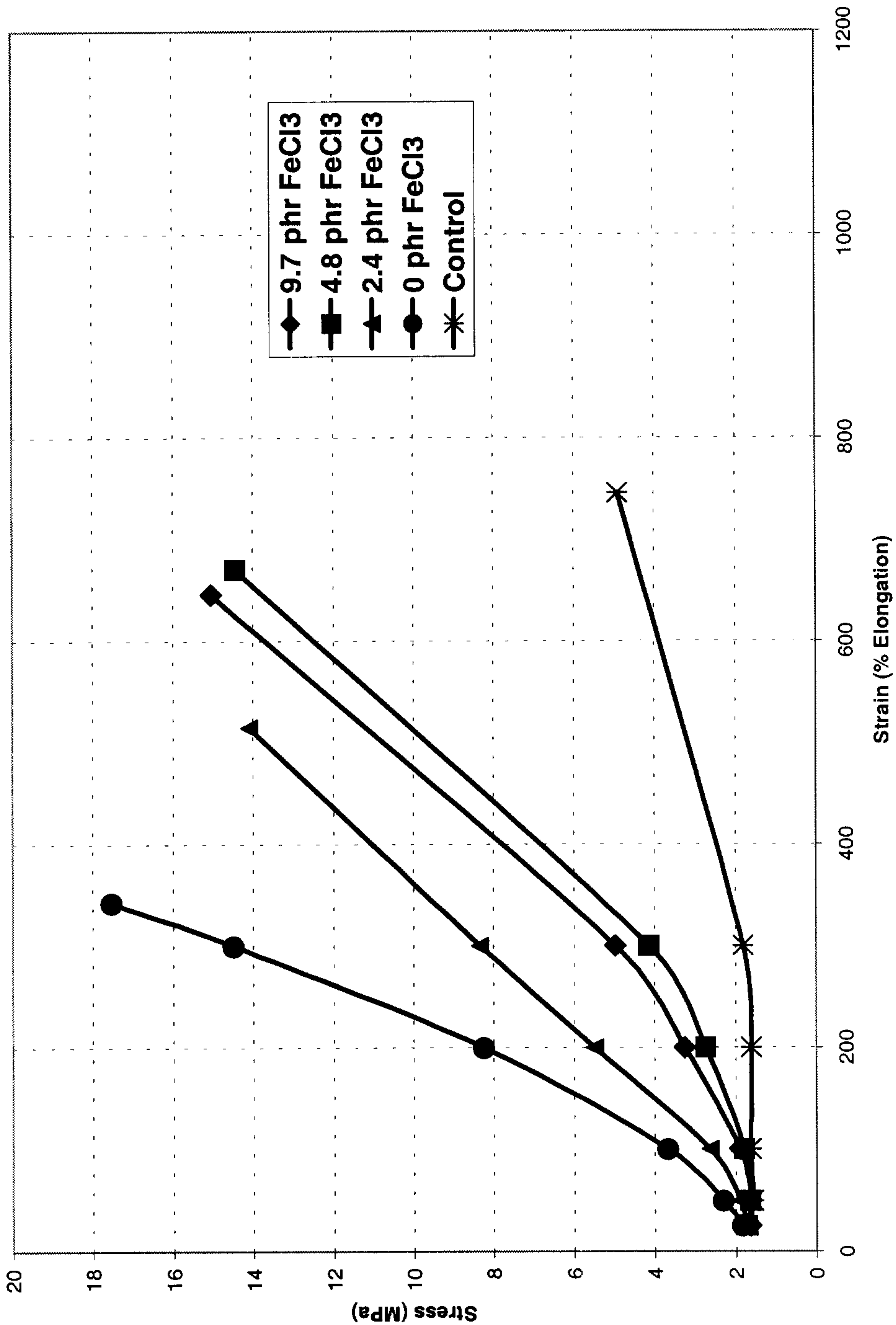


FIGURE 2.

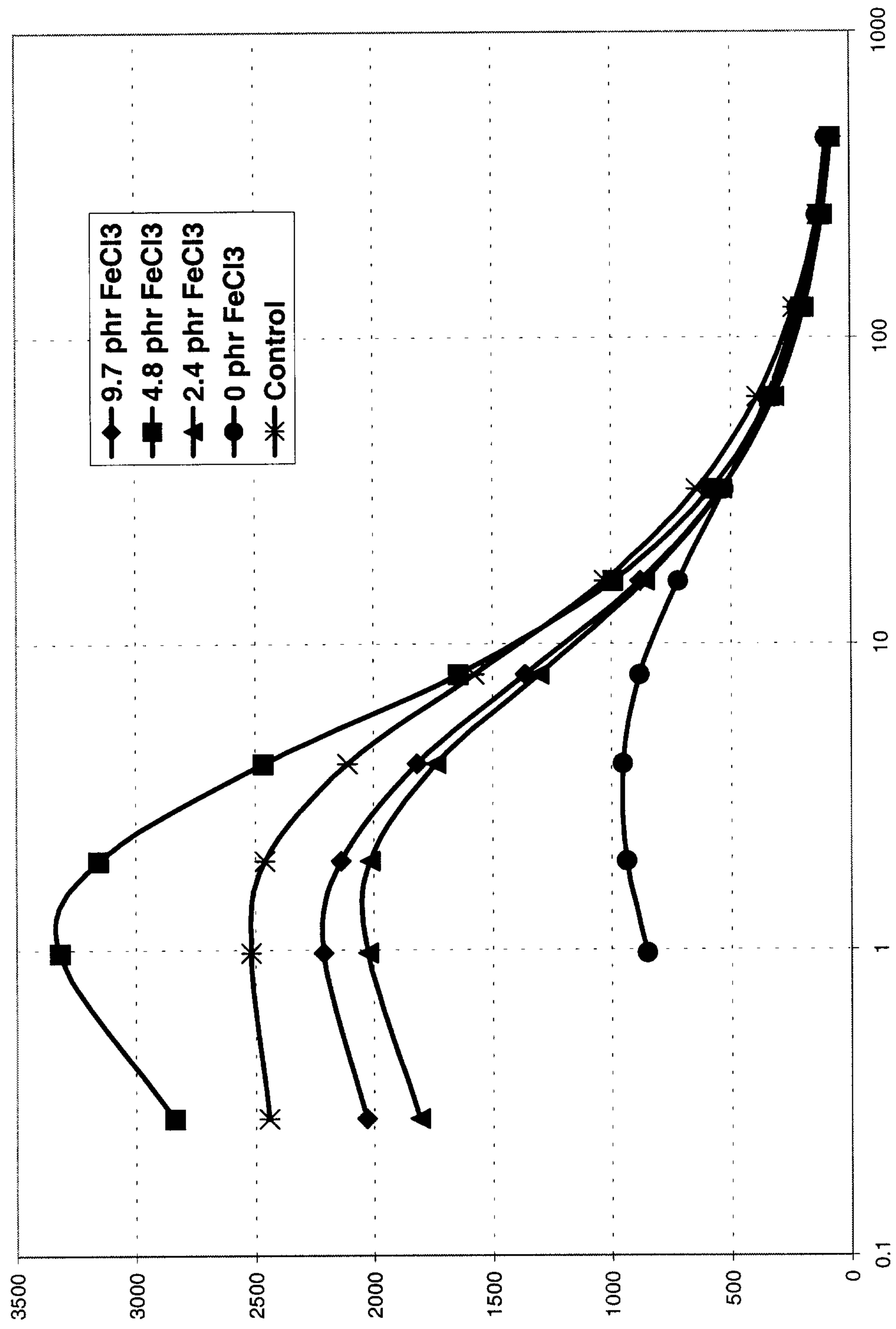


FIGURE 3.

