

1**3,679,619**
RIGID HALOGEN-CONTAINING RESIN
COMPOSITIONS

Christian H. Stapfer, Newtown, Pa., and William B. Racz, Highland Park, N.J., assignors to Cincinnati Milacron Chemicals, Inc., Reading, Ohio
No Drawing. Filed Dec. 11, 1970, Ser. No. 97,309
Int. Cl. C08f 45/04

U.S. Cl. 260—23 XA

11 Claims

ABSTRACT OF THE DISCLOSURE

Halogen-containing resin compositions containing an admixture of a lubricant and a synthetic silicate powder exhibit improved lubricity, stability and higher deflection temperatures.

This invention relates to lubricants for halogen-containing resins, resins lubricated therewith and methods of lubricating halogen-containing resins. More particularly, this invention relates to internal and external lubricants suspended on synthetic silicates, rigid polyvinyl halide resins containing the same and methods of lubricating rigid polyvinyl halide resins.

Lubricants for halogen-containing resins, such as polyvinyl halides, are generally classified as external or internal lubricants. External lubricants include materials which predominately reduce friction between the polymer melt and mechanical processing equipment in contact therewith. Paraffin oils and waxes as well as higher fatty acid amides are usually classified as external lubricants. Internal lubricants are those materials which predominately reduce the intermolecular friction within the polymer melt. Carboxylic acids, monocarboxylic acid esters and polyhydroxymonocarboxylic acid esters are usually classified as internal lubricants. Some materials exhibit both internal and external lubricating properties. Examples of compounds exhibiting internal and external lubricity are diesters of long chain monocarboxylic acids with polyhydric alcohols and long chain monohydroxyalcohols with dicarboxylic acids. These internal-external lubricants are more fully described in the application of Christian H. Stapfer, Ser. No. 755,736, filed Aug. 27, 1968, now U.S. Pat. No. 3,578,621.

One characteristic of a lubricant which substantially affects its performance, is the ability to rapidly and thoroughly disperse during blending. This is important since lubricants are usually added to the resin formulation with vigorous agitation and as a melt. Another important aspect of lubricants is the ability to be retained in resins during blending. Otherwise, effective lubricants frequently migrate to the surface during processing and are ejected from the resin. This phenomenon is referred to as "spewing" in the art.

It is known that the effectiveness of lubricants on resin formulations can be evaluated by measurement of rheological properties of the formulation. These properties are best studied by means of a torque rheometer consisting of a miniature mixer and a torque meter which measures the load on the mixer. The mixing forces developed within a sample of material at a certain temperature cause a deflection of a recording dynamometer. The deflection is recorded on a strip chart. This torque (expressed in meter-grams) is directly related to the viscosity of the melt being mixed. When a polymer of the vinyl type degrades, it cross-links rapidly and shows a sharp rise in its melt viscosity. The time for this to occur is a measure of the thermal stability under dynamic shear conditions.

2

A typical torque rheometer curve provides one skilled in the art with information as to the melting, the fusion, the flow and the cross-linking in the processing of the polymer tested.

5 Torque rheometer data has been evaluated by mathematical rheological interpretations and by rather simple pragmatic interpretations. The latter interpretations allow generalizations of various phenomena and relate the generalization to processability of the polymer melt tested.
10 The post fusion torque determined by rheometric testing is an extremely revealing value. Since post fusion torque is measured after the blend has melted, the value is controlled by the melt viscosity which is affected by internal and external lubricity. The viscosity of the melt has a substantial bearing on the effective stability of a given formulation, since melts with higher viscosities develop more heat during processing and consequently reduce the stability of the formulation.

15 It is generally accepted that a polymer exhibiting a long fusion time and low pre-fusion torque has good external lubricity whereas the contrary characteristics are indicative of good internal lubricity. Polymers which exhibit a long fusion time and high pre-fusion torque are generally accepted as having both internal and external lubricity. Long term heat stability is generally evaluated in the time in minutes, elapsed between the moment when the example is placed under dynamic shear and the moment the post fusion torque increases from the minimum value reached during the stable mixing.

20 30 It is an object of the present invention to provide a lubricant overcoming the disadvantages noted above.

25 It is a further object of the present invention to provide polyvinyl halide resins having improved lubricity and heat stability.

30 35 We have found that improved processability and long term heat stability of halogenated resins and particularly rigid polyvinyl chloride formulations are obtained when the lubricant of the resin formulation is incorporated in admixture with synthetic silicate powders. Suitable silicate 40 powders preferably have a combination of properties such as low bulk density, high absorptive capacity, varied particle size and shape and a high surface area. Their chemical constitution may vary as follows: 40-70% silica (SiO_2); 1 to 30% lime (CaO); 1 to 5% alumina (Al_2O_3); 45 1 to 2% iron oxide (Fe_2O_3); 0.1 to 20% magnesia (MgO); 1 to 2% alkalis (Na_2O+K_2O) and 10 to 20% volatile matter. The particle size of these synthetic silicate 50 55 powders usually ranges from 1 to 100 microns and the preferred range is between 20 and 50 microns. The absorptive properties exhibited by the synthetic silicate powders appear to be very important to the present invention. We have observed that natural silicates, such as diatomaceous earth, do not possess the necessary ability to absorb to be useful in practicing the present invention. The retention capacity of these mixed silicates allows absorption of lubricants up to 300% by weight based on the 60 65 silicates. In addition to the commercial advantage of transforming a low melting product into a fine free flowing powdery product, the novel combination improves both the lubricity and heat stability of formulations containing the novel product. Attempts substituting a natural silicate powder in admixture with the lubricant for the synthetic silicate admixture do not produce the improved results obtained when the synthetic silicates are used. The lubricating admixtures are prepared by simply blending the silicate powder with the lubricant. The silicate powder and the lubricant may be simultaneously introduced to a mixing vessel or one may be introduced into the other.

70 75 The simultaneous introduction of the silicate powder and lubricant is preferred, since it lends itself best to a continuous mixing operation.

3

The optimum improvement is obtained with balanced lubricants having both internal and external characters such as, stearamid waxes, dicarboxylic acid diesters, mono-carboxylic acid esters of diols and montan ester waxes. With these compounds higher pre-fusion torque, increased fusion time as well as prolonged heat stability result. The improvement is less noticeable when the lubricant is exclusively internal, such as with glycerol monostearate or exclusively external, such as with mineral oil. However, in all cases and regardless of the structure or character of the lubricant, the novel combination improves the heat stability of the formulation.

Silicates, alone, have no lubricating properties. However, the amount of synthetic silicates in the lubricating combination generally does not affect performance. The silicate lubricant ratio may vary from about 9:1 to about 1:9 without deleterious effects on the lubricating activity of the mixture, and preferably from 3:1 to 1:3. The recommended level of the lubricants of the present invention is from about 0.01 to 5 weight percent based on the resin and preferred range is from about 0.1 to 2.0 weight percent.

Examples of internal lubricants which are suitable for practicing the present invention include long chain acids and alcohols such as, stearic acid, nonadecanoic acid, arachidic acid, montanic acid, stearyl alcohol, carnaubyl alcohol, ceryl alcohol and montanyl alcohol; esters of polyhydric alcohols and short chain monocarboxylic acids, such as, glycerol monostearate, ethylene glycol dilaurate, 2-ethylhexane diol-1,3-distearate, ethylene glycol di-2-ethylhexanoate and octylene glycol dicaprylate and esters of dicarboxylic acids with short chain monohydroxy-alcohols, such as diisooctyl sebacate and dilauryl azelate.

Examples of external lubricants include high molecular weight paraffin waxes, such as Aristowax 165 and Montan wax ester and high molecular weight amide waxes such as ethylene distearamide. The diesters exhibiting both internal and external lubrication in the aforementioned Stapfer application including, for example, ethylene glycol distearate, distearyl azelate, distearyl maleate, distearyl sebacate and 2-ethylhexane-1,3-diol distearate are suitable for practicing the present invention.

The resins suitable for practicing the present invention are polyvinyl chloride, polyvinylidene chloride, copolymers containing at least 50 weight percent vinyl chloride or vinylidene chloride and other ethylenically unsaturated copolymerizable monomers and blends containing at least 50 weight percent polyvinyl chloride or vinylidene chloride with polymers of other ethylenically unsaturated compounds.

The rigid resin compositions for which the novel lubricating compositions are intended are substantially unplasticized resin formulations. As used herein, the term "rigid" is intended to describe resin formulations which are substantially unplasticized and are suitable for structural articles, such as, plastic pipe, containers, including clear bottles, and sheets. Plasticized resin formulations usually do not require the presence of lubricants since they do not develop stresses and shear forces occurring during the physical processing of rigid resin formulations.

We have also discovered that the novel lubricant combinations increase the deflection temperature of rigid polyvinyl chloride under load. The temperature, at which an arbitrary deformation occurs, when specimens are subjected to set testing conditions, can be determined by ASTM standard methods. We have found that rigid formulations lubricated with the novel silicate-lubricant mixtures of this invention exhibited heat distortion temperatures several degrees centigrade above those of similar formulations lubricated with the lubricant alone.

The following examples are presented as being illustrative of the present invention. The admixtures used in the following examples were prepared by blending the lubricant and synthetic silicate powder in a Henschel high speed blender for five (5) minutes.

4

EXAMPLE 1

A master batch containing 100 parts of a polyvinyl chloride homopolymer, 10 parts titanium dioxide and 1 part of di-n-butylin bis(isooctylthioglycolate) was prepared. A first test formulation of the master batch was lubricated with 1 weight percent of a mixture of 3 parts glycerol monostearate and 1 part of a synthetic silicate powder having an analysis of 54.3% SiO₂, 25.1% CaO, 3.6% Al₂O₃, 1.2% Fe₂O₃, 0.5% MgO, 1.3% (Na₂O+K₂O) and 14% volatile matter and 60 grams of this test formulation were processed on a torque rheometer manufactured by the Brabender Company at 180° C. and 40 r.p.m. When compared with a second test formulation of the master batch lubricated only with 0.75 weight percent of glycerol monostearate, the values developed are reported in Table I.

TABLE I

	Lubricant with silicate	Lubricant only ¹	Silicate only ¹
Parts total of lubricant mixture/100 parts resin	1.0	-----	1.0
Parts lubricant/100 parts resin	0.75	0.75	0.0
Fusion time in minutes	1.4	1.5	0.0
Pre-fusion torque in m./g.	1,500	1,700	2,000
Post fusion torque in m./g.	2,500	2,600	3,000
Stability in minutes	7.4	6.6	5.5

¹ For comparison purposes only.

This example demonstrates that the novel lubricants of the present invention improved internal lubrication and stability of the resin compositions.

EXAMPLE 2

Using the master batch and silicate powder of Example 1, the test of Example 1 was repeated except octylene glycol distearate was substituted for the lubricant of Example 1. Table II reports the values observed during the test.

TABLE II

	Lubricant with silicate	Lubricant only ¹	Silicate only ¹
Parts total lubricant mixture/100 parts resin	1.0	-----	1.0
Parts lubricant/100 parts resin	0.75	0.75	0.0
Fusion time in minutes	2.6	2.6	0.0
Pre-fusion torque in m./g.	1,000	1,200	2,000
Post fusion torque in m./g.	2,400	2,600	3,000
Stability in minutes	8.0	7.8	5.5

¹ For comparison purposes only.

EXAMPLE 3

A test formulation of the master batch was lubricated with 1 weight percent of a mixture of 3 parts ethylene distearamide and 1 part of a synthetic silicate powder having an analysis of 52.9% SiO₂, 22.6% CaO, 3.6% Al₂O₃, 1.2% Fe₂O₃, 0.4% MgO, 1.3% (Na₂O+K₂O) and 14% volatile matter. Another test formulation was prepared from the master batch, which was lubricated with 0.75 weight percent ethylene distearamide alone. The two test formulations were processed at 180° C. at 50 r.p.m. in a torque rheometer. Table III presents the results.

TABLE III

	Lubricant with silicate	Lubricant only ¹
Parts total lubricant mixture/100 parts resin	1.0	-----
Parts lubricant/100 parts resin	0.75	0.75
Fusion time in minutes	1.4	0.6
Pre-fusion torque in m./g.	1,000	1,300
Post fusion torque in m./g.	2,475	2,550
Stability in minutes	5.5	4.2

¹ For comparison purposes only.

EXAMPLE 4

Using the master batch and the silicate powder, the test of Example 3 was repeated except paraffin wax was

5

substituted for ethylene distearamide as the lubricant. Table IV reports the values observed.

TABLE IV

	Lubri- cant with silicate	Lubri- cant only ¹
Parts total lubricant mixture/100 parts resin	1.0	
Parts lubricant/100 parts resin	0.75	0.75
Fusion time in minutes	0.5	0.5
Pre-fusion torque in m./g.	900	1,200
Post fusion torque in m./g.	2,625	2,750
Stability in minutes	3.8	3.4

¹ For comparison purposes only.

Examples 3 and 4 demonstrate that the novel lubricants of the present invention improve the external lubrication and stability of the resin composition. 15

EXAMPLE 5

Using the silicate of Example 3 and the master batch, three test formulations were prepared with a lubricant combination of distearylazelate and paraffin used at the 0.75 weight percent level based on the resin. In test formulation "A," three parts of the lubricant combination were used in admixture with 1 part of the silicate powder. In test formulation "B," the lubricant combination was used alone and in test formulation "C" the lubricant combination was added to the master batch separately from the silicate which was used at a level equal to that in "A." Following the procedure of Example 3, the three formulations were tested and the results are reported in Table V.

TABLE V

Lubricant	How applied	Lubricant level	Fusion time, minutes	Pre-fusion torque, m./g.	Post fusion torque, m./g.	Stability, minutes
A-----	Distearylazelate/paraffin - In admixture with silicate powder-----	0.75	0.8	1,400	2,500	3.7
B-----	do - Alone-----	0.75	0.8	1,600	2,600	2.8
C-----	do - Introduced separately with silicate powder-----	0.75	0.8	1,600	2,600	2.8

¹ For comparison purposes only.

The test results of Example 5 demonstrate that the lubricant does not improve the properties of resins if the silicate is omitted or the silicate powder and lubricant are separately introduced into the formulation.

EXAMPLE 6

Using the master batch and the silicate powder of Example 1 the ratio of lubricant to silicate powder in the lubricant combinations was varied from 3:1 to 1:3. The test formulations were processed according to the procedure of Example 1 and the results are presented in the following table.

TABLE VI

Lubricant		Observed	
Name	Ratio to silicate powder	Level, percent	Stability, minutes
Glycerol monostearate-----	3:1	0.75	7.4
	1:1	0.75	7.4
	1:3	0.75	7.4
Octyleneglycol distearate-----	3:1	0.75	8.0
	1:1	0.75	8.0
	1:3	0.75	8.0

The processability of the test formulations reported in Table VI were not noticeably different and stability was consistent as noted above.

EXAMPLE 7

Following the procedure of ASTM standard method D648-56, two rigid polyvinyl chloride formulations were compared. One formulation consisted of 100 parts polyvinyl chloride homopolymer, 1.0 part di-n-butyltin bis(isooctylthioglycolate) and 2.67 parts of a mixture of 2 parts distearylazelate with 0.67 part of the silicate powder described in Example 3. The other formulation consisted of 100 parts of the same polyvinyl chloride homopolymer, 1.0 part di-n-butyltin bis(isooctylthiogly-

6

colate) and 2.0 parts distearylazelate alone. A sample of each formulation was immersed in an oil bath under a load of 18.5 kg./cm.² and the temperature was slowly increased until a deflection of 0.25 mm. was observed. The sample lubricated with the mixture of lubricant and silicate reached a temperature of 174° C. before the test deflection was reached while the sample containing the lubricant alone developed the test deflection at 172° C. These same results were obtained upon repeating the test.

We claim:

1. A halogen-containing resin composition selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, copolymers containing at least 50 weight percent vinyl chloride or vinylidene chloride and other ethylenically unsaturated copolymerizable monomers and blends containing at least 50 weight percent polyvinyl chloride or vinylidene chloride with polymers of other ethylenically unsaturated compounds containing, as a lubricant, a preblended admixture of a lubricant and a highly absorptive synthetic silicate powder, whereby said resin composition has lower prefusion and postfusion torque values than said resin having a lubricant alone, silicate powder alone or wherein said lubricant and silicate powder are not preblended.
2. The composition of claim 1 wherein said halogen-containing resin contains a major amount of polymerized vinyl chloride.
3. The composition of claim 2 wherein the admixture comprises the lubricant and synthetic silicate powder in a weight ratio of 9:1 to 1:9 and the synthetic silicate powder

has a composition comprising about 40 to 70% SiO_2 , 1 to 30% CaO , 1 to 5% Al_2O_3 , 1 to 2% Fe_2O_3 , 0.1 to 20% MgO , 1 to 2% $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ and 10 to 20% volatile matter.

4. The composition of claim 3 wherein the halogen-containing resin is polyvinyl chloride, contains about 0.01 to 5 weight percent of the admixture and the weight ratio is about 3:1 to 1:3.

5. The composition of claim 4 wherein the lubricant is at least one material selected from the group consisting of stearic acid, nonadecanoic acid, arachidic acid, montanic acid, stearic alcohol, carnaubyl alcohol, cetyl alcohol, montanyl alcohol, glycerol monostearate, ethylene glycol dilaurate, ethylene glycol di-2-ethylhexanoate, octylene glycol dicaprylate, diisooctyl sebacate dilauryl azelate, 2-ethylhexanediol-1,3-distearate, high molecular weight paraffin waxes, high molecular weight amide waxes, ethylene glycol distearate, distearyl maleate and distearyl sebacate.

6. The composition of claim 4 wherein the lubricant is selected from the group consisting of dialkyl maleates having 18-25 carbon atoms in each alkyl group and alcohols containing 18-25 carbon atoms.

7. The composition of claim 6 wherein the lubricant is a mixture of synthetic alcohol having 20-23 carbon atoms.

65 8. The composition of claim 7 wherein the silicate has a composition of about 54% SiO_2 , 25% CaO , 3½% Al_2O_3 , 1% Fe_2O_3 , 15% MgO , 1.5% $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ and 14% volatile matter in a ratio of 1 part silicate to 3 parts of the lubricant.

70 parts of the lubricant.

9. The composition of claim 6 wherein the lubricant is dialkyl maleate; the silicate has a composition of about 54% SiO_2 , 25% CaO , 3½% Al_2O_3 , 1% Fe_2O_3 , 15% MgO , 1.5% $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ and 14% volatile matter and 75 the ratio of lubricant to silicate is about 3:1.

10. The composition of claim 9 wherein the lubricant is distearyl maleate.

11. The composition of claim 6 wherein the synthetic silicate powder has a composition of about 54% SiO₂, 25% CaO, 3 1/2% Al₂O₃, 1% Fe₂O₃, 15% MgO, 1.5% (Na₂O+K₂O); the lubricant is stearyl alcohol and the ratio of lubricant to synthetic silicate powder is 3:1.

References Cited

UNITED STATES PATENTS

3,578,621	5/1971	Stapler	260—31.6
3,324,060	6/1967	Scopp et al.	260—23
3,266,924	8/1966	Haeske et al.	106—308

2,993,022	7/1961	Coler	260—32.6
3,382,199	5/1968	Scullin	260—23

OTHER REFERENCES

5 The Condensed Chemical Dictionary, 6th edition, Reinhold Pub. Corp., New York, 1961, pp. 759, 760 and 1241.

LEWIS T. JACOBS, Primary Examiner

10 J. H. DERRINGTON, Assistant Examiner

U.S. CL. X.R.

260—28.30, 31.6 R, 31.8 R, 32.6 R, 33.4 R, 41 A