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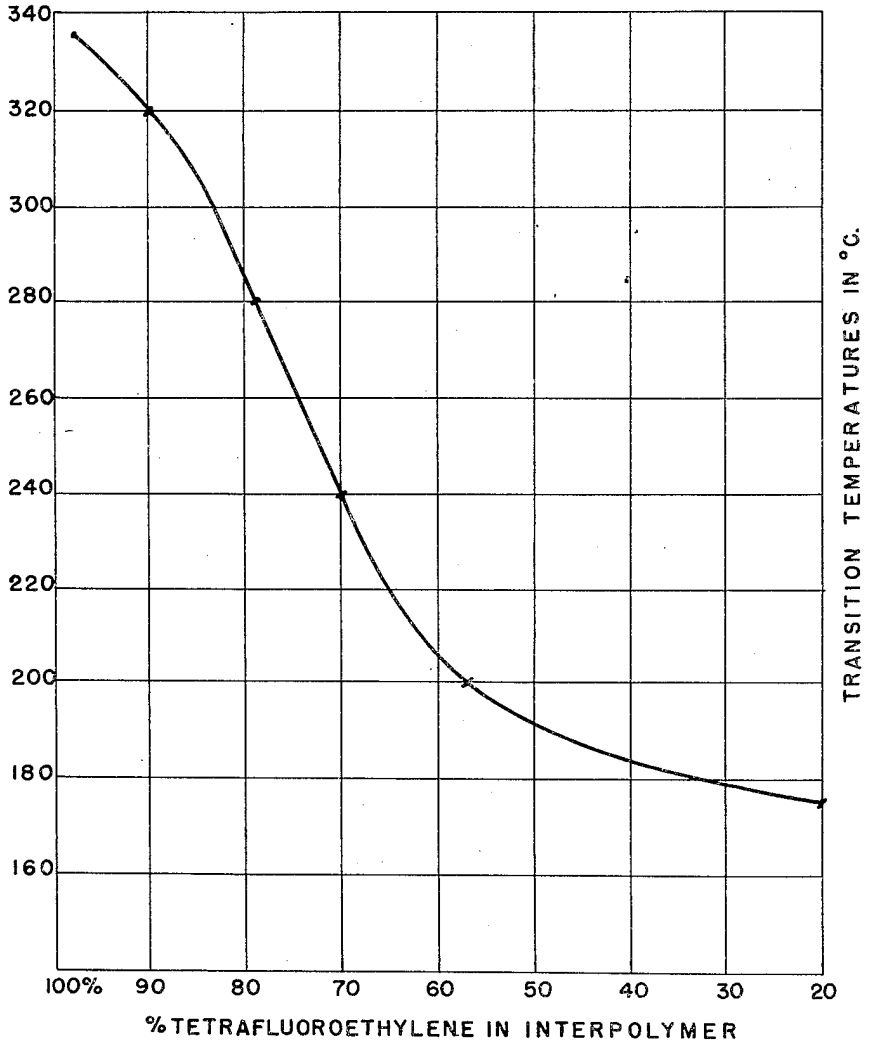

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THICKENED OILS AND GREASES

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This invention relates to thickened oils and greases obtained from fluorocarbon oils and interpolymers of tetrafluoroethylene and chlorotrifluoroethylene, and to methods of preparing such thickened oils and greases.

Substantially completely fluorinated hydrocarbon oils, that is, hydrocarbon oils which have been fluorinated to such an extent that substantially all of the hydrogen atoms of the compounds in the oils have been replaced by fluorine, are valuable as lubricants and heat transfer media under extremely corrosive conditions because they are stable and inert to most chemicals. Such fluorinated oils and methods of preparing them are disclosed in Ind. and Eng. Chem., vol. 39, No. 3, March 1947, on pages 290 to 292, 292 to 298, 319 to 329, 343 to 345, 350 to 352, and 352 to 354. Such completely fluorinated hydrocarbon oils are sometimes, for convenience, referred to herein as fluorocarbon oils.

The fluorocarbon oils have the disadvantage that their viscosity rapidly decreases with increase in temperature, much more rapidly than hydrocarbon oils, whereby they become too thin to be practical for lubrication and some other uses at high temperatures. The change in viscosity of an oil with change in temperature is indicated by the viscosity index. Therefore, it is desirable to improve the viscosity index of the fluorocarbon oils so as to render them useful over a wider range of temperatures and particularly at higher temperatures. Also, it is frequently desirable to provide greases which will have the characteristic inertness to corrosive chemicals of the fluorocarbon oils and which can be used under highly corrosive conditions and at high temperatures. However, the usual thickening agents, employed in making greases from hydrocarbon oils, do not have the desired inertness to corrosive chemicals and are incompatible with the fluorocarbon oils. Accordingly, the improvement of the viscosity index of the fluorocarbon oils and the preparation of suitable corrosion-resistant greases therefrom have presented serious problems.

Polymerized tetrafluoroethylene and the methods of preparing it are disclosed and claimed in Patent No. 2,230,654, to Plunkett. It is generally obtained as a white or brown powder or a jelly which rapidly changes to a powder. It is insoluble in all known solvents, is inert to the usual chemical reagents and does not burn. It is a crystalline material which undergoes a reversible transition at 327° C. and above whereby it becomes less crystalline and somewhat amorphous and loses much of its tensile strength but does not become liquid or fluid, otherwise retaining its physical form and being deformable only

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slowly at high pressures. Also, at temperatures of 327° C. and above, it will sinter, that is, coalesce into a solid mass, but it has no true melting point. It is immiscible with and is not affected by hydrocarbon oils and is not softened or swelled by such oils.

Polymerized cholorotrifluoroethylene and the process for preparing it are disclosed in British Patent 465,520, complete accepted May 3, 1937, issued to I. G. Farbenindustrie Aktiengesellschaft. It is generally similar to polymerized tetrafluoroethylene in its physical and chemical properties. Its chlorine constitutes a substituent which may be subject to attack by certain chemicals, but the polymer is resistant to attack by most chemicals. It appears to have a transition point somewhat lower than polymerized tetrafluoroethylene. Such transition point has not been determined, but has been estimated to be approximately 225° C. It is harder but has a lower softening point than polymerized tetrafluoroethylene and can be molded, extruded and bonded to itself by pressing at about 100 to 200 lbs./sq. in. while heating to 225° C. and above. It is not affected by hydrocarbon oils and is immiscible and insoluble therein.

Interpolymers of tetrafluoroethylene and chlorotrifluoroethylene may be made by polymerizing mixtures of such monomers in any desired proportions in accordance with the process disclosed by Brubaker, in Patent No. 2,393,967. The properties of the interpolymers are generally intermediate those of polymerized tetrafluoroethylene and polymerized chlorotrifluoroethylene, varying with the proportions of tetrafluoroethylene in the mixture from which they are prepared, and more closely approaching the properties of polymerized tetrafluoroethylene as the proportion of tetrafluoroethylene is increased, in other words, as their composition more closely approaches polymerized tetrafluoroethylene. Such interpolymers are not affected by hydrocarbon oils and are immiscible and insoluble therein. Attempts to incorporate such interpolymers into petroleum oil, by heating mixtures thereof at 325° C. to 330° C., have been unsuccessful.

J. Denny Compton, Joseph W. Justice and Carl F. Irwin, in their application Serial No. 37,528, filed July 8, 1948, for "Plasticized Polymers," now Patent No. 2,510,078, patented June 6, 1950, disclose that polymerized tetrafluoroethylene, polymerized chlorotrifluoroethylene and interpolymers of tetrafluoroethylene and chlorotrifluoro ethylene can be plasticized, i. e., rendered more plastic at lower temperatures, by heating with certain proportions of fluorocarbon oils at temperatures between 150° C. and 400° C. By such

procedure, however, neither polymerized tetrafluoroethylene, nor polymerized chlorotrifluoroethylene can be incorporated in a fluorocarbon oil in a proportion to provide thickened oils or greases, such procedure resulting solely in the production of plasticized polymers even when an excess of the fluorocarbon oil is employed.

George E. Holbrook, in his application Serial No. 37,529 filed July 8, 1948, for "Polymer Compositions," now Patent No. 2,510,112 patented June 6, 1950, and also Compton, Justice and Irwin, in their application above referred to, disclose that greases, composed of colloidal polymerized tetrafluoroethylene, stably suspended in a fluorocarbon oil, may be obtained by coagulating an aqueous dispersion of colloidal polymerized tetrafluoroethylene in the presence of certain proportions of fluorocarbon oil at temperatures of from about 0° C. to about 100° C. with stirring. While such greases are valuable corrosion-resistant materials and have valuable lubricating properties, their consistency decreases with increase in temperature, particularly at high temperatures, at a rate which is undesirable for some purposes. Furthermore, such greases tend to be converted irreversibly to plastic materials at high temperatures and particularly at temperatures of from about 325° C. to about 400° C.

It is a general object of my invention to provide methods for improving the properties of fluorocarbon oils. A specific and particular object is to provide methods for preparing greases from fluorocarbon oils. Further objects are to provide new compositions of matter which are thickened oils and greases composed of fluorocarbon oils and interpolymers of tetrafluoroethylene and chlorotrifluoroethylene. Other objects are to provide new and improved compositions of matter. Still other objects are to advance the art. Still further objects will appear hereinafter.

The above and other objects may be accomplished in accordance with my invention which comprises heating a mixture of a substantially completely fluorinated hydrocarbon oil, distilling at temperatures in the range of from about 50° C. to about 300° C. at 10 mm. Hg pressure, and from about 0.5% to about 20% by weight of a solid (solid at atmospheric temperatures) interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, containing from 98.5% to 20% tetrafluoroethylene, at temperatures between 175° C. and about 400° C. with stirring, continuing such heating until the mixture becomes clear and homogeneous in appearance and more viscous, and then cooling. By such procedure, the mixture of interpolymer particles and fluorocarbon oil is converted to an apparently homogeneous thickened oil or grease, depending upon the proportion of the interpolymer in the product.

Mixtures of interpolymer powder and fluorocarbon oil, prepared by thorough mechanical mixing at room temperatures, are oily and unstable, the polymer particles rapidly settling out on standing and being separable from the oil by filtration or decantation. When such mixtures are examined under an ordinary 450 power microscope with ordinary lighting and under a phase contrast microscope at 376 magnification, the particles of polymer appear to be present in their original form as small discrete particles. By "ordinary lighting," I mean diffuse substage illumination that is ordinarily employed with simple microscopes. A mixture of from 15% to 20% of interpolymer powder in fluorocarbon oil is so viscous at room temperature that is is difficult to stir, but thins considerably at 50° C. to 60° C. and becomes a thin slurry at 100° C. As the temperature is increased, the viscosity appears to gradually decrease and the particles of interpolymer become more finely subdivided, increasing the cloudiness of the mixture, until, at a transition temperature between 175° C. and about 335° C., the mixture rapidly becomes clear and homogeneous in apearance and so viscous that it is difficult to stir; then, upon cooling, it is found that the mixture has been converted to an opaque grease which changes in consistency only slowly on heating until its transition temperature is reached, at which point it again becomes very sticky and viscous. The greases may be mulled, in the manner commonly employed with other greases, in order to give them a better, particularly a smoother, consistency.

The thickened oils and greases, obtained in accordance with my invention, are homogeneous in appearance and stable, that is, they do not separate in use or in storage over long periods of time, at least several months, and the interpolymer cannot be separated from the oil by filtration. Also, they have the appearance, feel and rheological properties characteristic of thickened oils and greases prepared from hydrocarbon oils. While the greases are somewhat opaque, separate particles cannot be observed in them or in the thickened oils when they are examined by the naked eye or under an ordinary 450 power microscope employing ordinary lighting. However, when the greases of my invention are examined under a phase contrast microscope at 376 magnification, the polymer appears in the form of stringy, fibrous, apparently coalescent masses or agglomerates, and no separate, unattached particles of polymer were observed. Such stringy masses appear to be elastic and are not broken down to small, discrete and unattached particles by vigorous grinding or mulling. Sometimes, the fluorocarbon oil employed will contain a small amount of crystalline material, dust and the like which is observable under the dark-field microscope, and such materials should not be confused with the polymer. The fluorocarbon oil in the compositions can be largely separated from the interpolymer by distillation or by repeated extractions with a solvent for the fluorocarbon oil, such as, trifluorotrichloroethane.

My compositions are inert to most chemicals and are particularly adapted for use as lubricants and heat transfer media where corrosive conditions are encountered and at high temperatures up to their transition temperatures or up to the boiling ranges of the fluorocarbon oils, whichever is the lower. The products of my invention are also useful for adhering massive interpolymer to itself or to metal, as by coating one or both of the surfaces thereof with a thin layer of the thickened oil or grease, pressing the surfaces together, and heating to the transition temperature of the thickened oil or grease until the massive interpolymer has absorbed sufficient of the fluorocarbon oil to convert the thickened oil or grease to a plastic material. In such use as an adhesive, it will generally be preferred to use a product containing an interpolymer having a composition approximating the composition of the massive interpolymer.

The thickened oils of my invention have an advantage over the fluorocarbon oils from which they are made in that the thickened oils have an improved viscosity index; that is, their vis-

cosity changes less rapidly with change in temperature and they are more viscous at higher temperatures, so that they are useful over a greater range of temperatures and at higher temperatures. The greases of my invention are particularly remarkable in that they show a smaller change in consistency (viscosity) over a wide range of temperatures than comparable hydrocarbon greases, even though the fluorocarbon oils show a very much larger change in viscosity over such temperature range than the hydrocarbon oils. The greases of my invention melt and become very sticky and viscous at their respective transition temperatures, the temperatures at which mixtures of the respective interpolymers and fluorocarbon oil are converted to greases, and continue to be sticky and viscous at temperatures up to about 100 C. above their transition temperatures. The thickened oils and greases may be heated to or above their transition temperatures and, upon cooling, will revert to their original condition, unless the temperatures and other conditions are such as to materially alter their composition, as by distilling off fluorocarbon oil or decomposing the fluorocarbon oil or the interpolymer or both.

The substantially completely fluorinated hydrocarbon oils (fluorocarbon oils), which may be employed in accordance with my invention, are those which have a distilling range at 10 mm. Hg pressure within the range of from about 50° C. to about 300° C. (about 150° C. to about 460° C. at atmospheric pressures). The term "substantially completely fluorinated" means that substantially all of the hydrogen atoms of the compounds in the hydrocarbon oil have been replaced by fluorine so that the fluorinated oil contains at least 75% chemically combined fluorine. These fluorocarbon oils may be obtained by fluorinating a hydrocarbon oil by methods known to the art and then fractionating the fluorinated oil, usually at 10 mm. Hg pressure, to obtain products of desired boiling range. The hydrocarbon oils, employed for preparing the fluorocarbon oils, are mixtures of hydrocarbons and may be naturally occurring mineral oils, such as paraffinic base, naphthenic base or highly aromatic petroleum oils, usually highly refined, or synthetic hydrocarbon oils of similar composition, such as the Fischer-Tropsch oils. Preferably, the hydrocarbon oils are composed wholly or mainly of aliphatic hydrocarbons. Usually, the hydrocarbon oil is vaporized, the vapors diluted with inert gas, and the mixture then passed over a fluorinating agent, such as cobalt trifluoride. Representative fluorocarbon oils and methods for preparing them are disclosed in the articles appearing in Ind. and Eng. Chem., vol. 39, No. 3, March 1947 on pages 290 to 292, 292 to 298, 319 to 329, 343 to 345, 350 to 352 and 352 to 354. The fluorocarbon oils, employed in the following examples, were prepared by the process disclosed in the article by Irwin et al., appearing on pages 350 to 352, inclusive, of such publication.

While a fluorocarbon oil fraction, distilling over the full range of from about 50° C. to about 300° C. at 10 mm. pressure, may be employed, it will generally be desirable to employ fractions distilling over narrower ranges within such broad range. It will usually be preferred to employ fluorocarbon oil fractions having distilling ranges wholly above 80° C. at 10 mm. (200° C. at atmospheric pressures) and particularly those having distilling ranges between 80° C. and about 240° C. at 10 mm. (200° C. to 400° C. at atmospheric pressure). I specially prefer to employ fractions having distilling ranges falling in the range of from about 130° C. to about 240° C. at 10 mm. The use of fluorocarbon oils, having constituents distilling below the temperature of treatment, will require the use of pressures to prevent the loss of oil by vaporization during the processing or, alternatively, the use of excess amounts of oil to allow for that lost by vaporization. The viscosity of the fractions of fluorocarbon oil varies with their distilling range, those distilling at higher temperatures having higher viscosities. The viscosities of the thickened oils and the hardness of the greases will vary with the original viscosity of the fluorocarbon oil employed and with the proportion of interpolymer incorporated therein, increasing with increase in the original viscosity of the fluorocarbon oil and with increase in the proportion of the interpolymer.

The interpolymers, which may be employed in accordance with my invention, are interpolymers of tetrafluoroethylene and chlorotrifluoroethylene containing from 20% to 98.5% tetrafluoroethylene; in other words, they are formed by the interpolymerization of mixtures of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene constitutes from 20% to 98.5% by weight of the mixture and the chlorotrifluoroethylene constitutes from 80% to 1.5% by weight of the mixture. Interpolymers, containing proportions of tetrafluoroethylene outside of such range, appear to be inoperable to produce thickened oils and greases in accordance with my invention. Variations, in the proportions of tetrafluoroethylene to chlorotrifluoroethylene in the interpolymer (conveniently expressed as % tetrafluoroethylene in the interpolymer), produce variations in the viscosities or consistencies of my products. Interpolymer, containing about 70% tetrafluoroethylene, appears to have the greatest effect and to produce the highest viscosity and stiffest greases, such effect decreasing as the per cent of tetrafluoroethylene in the interpolymer is either increased or decreased. This effect, of variation in the composition of the interpolymer, is quite pronounced in the fluorocarbon oils of low viscosity, but decreases with increase in the viscosity of the fluorocarbon oil employed, being relatively small in fluorocarbon oils whose distilling range at 10 mm. pressure is within the range of from about 190° C. to about 300° C.

The interpolymers may be made by methods known to the art, particularly by the methods disclosed by Brubaker in Patent No. 2,393,967; that is, under pressure at slightly elevated temperatures in the presence of an aqueous solution of an alkali persulfate (preferably, ammonium persulfate) with or without an alkaline buffer. Variations in the conditions of making the interpolymers result in slight variations in their properties, such as the transition temperatures and viscosity or consistency of the products of my invention.

The interpolymers are ordinarily obtained as powders, usually, as coarse granular powders. They may be used in such condition in my invention or they may be prepared in a more finely divided condition by carrying out the polymerization in a violently agitated system or by subjecting the interpolymer to a mechanical subdivision step such as micropulverization. The required period of heating at the transition tem-

perature to complete the conversion will be shorter with the more finely divided interpolymer.

In order to obtain the products of my invention, a mixture of the fluorocarbon oil and the interpolymer, in the desired proportions, is heated to a temperature of from about 175° C. to about 400° C. and to at least the transition temperature, continuing such heating until the mixture is converted to a clear and homogeneous mass and its viscosity noticeably increases, and then cooling and, if desired, mulling. Usually, the temperatures employed will be somewhat above the transition temperatures so as to allow for inaccuracies in measuring and controlling the temperatures and in determining the transition temperatures and for fluctuations in the heating. The minimum or transition temperature will vary with the composition of the interpolymer, that is, with the proportion of tetrafluoroethylene in the interpolymer, substantially in accord with the curve in Fig. 1 of the accompanying drawings. The exact transition temperature in any case can be determined by slowly heating the mixture of fluorocarbon oil and the selected interpolymer, in powder form, with stirring, whereupon the mixture will become progresively thinner with increase in the temperature until suddenly, when the transition temperature is reached, the mixture becomes clear and homogeneous in appearance and more viscous. When the interpolymer is in finely divided form, the change from a thin mixture to a clear and apparently homogeneous, more viscous mass, is substantially instantaneous at the transition temperature and higher temperatures and hence, it is necessary to continue heating at such temperatures for only a few minutes to ensure completion of the conversion.

Temperatures materially above 400° C. tend to cause objectionable decomposition of the fluorocarbon oil and of the interpolymer and hence should ordinarily be avoided. When the interpolymer employed contains about 20% tetrafluoroethylene, the transition temperature is about 175° C. As the proportion of tetrafluoroethylene in the interpolymer is increased, the transition temperature rises slowly to about 181° C. for interpolymer containing 34% tetrafluoroethylene and to about 200° C. for interpolymer containing 57% tetrafluoroethylene and then more rapidly to about 240° C., 280° C., 320° C. and 335° C. for interpolymers containing 70%, 79%, 90% and 98.5% tetrafluoroethylene, respectively. The transition temperatures are critical, For example, when a mixture of about 2 grams of interpolymer (containing about 60% tetrafluoroethylene and about 40% chlorotrifluoroethylene) and about 20 grams fluorocarbon oil having a distilling range of about 150–170° C. at 10 mm. was heated at 145–150° C. for more than 26 days, there was no apparent change in the mixture which remained a mixture, or slurry, of clear fluorocarbon oil and particles of slightly softened interpolymer.

While interpolymers, containing from 98.5% to 20% tetrafluoroethylene, may be used, it will generally be desirable to use those containing 34% or more tetrafluoroethylene because of their higher transition temperatures which render the products useful at higher temperatures and they are more readily incorporated into the fluorocarbon oils to form products of smooth or uniform consistency. I particularly prefer to employ interpolymers containing 57% or more tetrafluoroethylene. Also, preferably, the interpolymers should not contain more than about 90% tetrafluoroethylene.

On pages 81 to 85, inclusive, of ASTM Bulletin, No. 147 for August of 1947, there is described a micro penetration test for empirically measuring the consistency of small samples of grease, in which the penetration values are the distances in tenths of a millimeter to which the micro cone will penetrate the grease in 5 seconds at specified temperatures, such as 77° F., and a curve for converting the values, thus obtained, to standard penetration values. The ASTM penetration values given herein are standard penetration values which were determined by such method.

A thickened oil of my invention may be obtained by incorporating from about 0.5% to about 2% of the interpolymer into the fluorocarbon oil by the procedure above described. Greases of my invention, having ASTM penetration values of from well over 350 to about 25 at 77° F., may be obtained by incorporating from about 2% to about 20% of interpolymer in fluorocarbon oil. In the range of about 2% interpolymer in the fluorocarbon oil, the thickened oils and the greases closely approach each other in consistency and, whether the product is a thickened oil or a grease, will depend upon the thickening effect of the particular interpolymer and the original viscosity of the fluorocarbon oil employed. For example, a thickened oil may be obtained containing slightly more than 2% of interpolymer if the interpolymer is one having a relatively low thickening effect, such as those containing 90% or more or 57% or less of tetrafluoroethylene, and if the fluorocarbon oil is one having a relatively low viscosity, such as those distilling at 130–150° C./10 mm. or lower. Similarly, greases, containing slightly less than 2% of interpolymer, may be obtained if the interpolymer has a high thickening effect, such as those containing approximately 70% tetrafluoroethylene, and the fluorocarbon oil is one which originally has a high viscosity, such as those distilling in the range of from about 170° C. to about 300° C. at 10 mm. The effects, of variations in the viscosities of the fluorocarbon oil employed and in the composition of the interpolymer, on the ASTM penetration values are indicated in the following Table I, in which Oil A is a fluorocarbon oil having a distilling range of 130–300° C./10 mm., Oil B is a fluorocarbon oil having a distilling range of 150–170° C./10 mm., and Oil C is a fluorocarbon oil having a distilling range of 190–210° C./10 mm.:

Table I

Oil	Composition of Interpolymer		Interpolymer, Per Cent in Oil	ASTM Penetration Values	
	Per Cent C_2F_4	Per Cent C_2F_3Cl		77° F.	210° F.
A	57	43	13	170	
B	57	43	9.5	270	355
B	60	40	8	340	(1)
B	70	30	8	273	345
B	90	10	8	350	(1)
B	60	40	12	269	346
B	70	30	12	173	315
B	90	10	12	278	(1)
C	60	40	8	210	385
C	70	30	8	173	340
C	90	10	8	190	342
C	60	40	12	180	260
C	70	30	12	130	198
C	90	10	12	135	201

[1] Too thin to measure.

In order to illustrate my invention, preferred modes of carrying the same into effect and advantageous results obtained thereby, the following examples are given in which the proportions

and parts are by weight, except where otherwise specifically indicated:

EXAMPLE 1

0.2 gram of interpolymer (57% tetrafluoroethylene and 43% chlorotrifluoroethylene), in the form of a dry powder, and 3 g. of fluorocarbon oil (distilling range 150–170° C./10 mm.) were placed in a test tube and slowly heated while being stirred. As the temperature increased, the contents of the tube became thinner and thinner until, suddenly at 200° C., it appeared that a gelatinous film stuck to the walls of the tube and the rest of the contents became clear, homogeneous, highly viscous and sirupy. The material was allowed to cool, whereby it lost its viscous sirupy consistency, became a curdy grease, and did not revert to its original slurry form. Such grease was found to be a satisfactory lubricant for stopcocks as it does not tend to roll up when the stopcocks are warmed. It can be given a smoother consistency by milling.

EXAMPLE 2

4 grams of interpolyer (57% of tertafluoroethylene and 43% of chlorotrifluoroethylene), in the form of a dry powder, was heated with 38 g. of fluorocarbon oil (distilling range 150° C. to 170° C./10 mm.). This heating was done very slowly and with constant stirring. As the temperature was increased, the slurry became thinner and thinner until, at about 200° C., the entire mass suddenly became viscous and homogeneous. Upon cooling and milling, an excellent grease resulted. This grease was very resistant to the attack of chemicals such as chlorine, wet HCl, and caustic and is of very great value as a lubricant in circumstances where such corrosive materials are present. It was practically insoluble in most organic solvents, such as CCl_4, acetone, perchloroethylene and o-dichlorobenzene. This grease had A. S. T. M. penetration values of 270 at 77° F. and 355 at 210° F. A comparable, commercial, calcium base hydrocarbon grease (apparently composed of about 10–30% of calcium soaps of fatty acids in a medium viscosity petroleum oil) had A. S. T. M. penetration value of 210 at 77° F. and 305 at 210° F.

EXAMPLE 3

Employing the process of Example 2, from about 0.5% to about 2.0% of the interpolymer, described in Example 2, was incorporated into each of two fractions of fluorocarbon oil, one having a distilling range of 130° C. to 150° C./10 mm. and the other having a distilling range of 150° C. to 170° C./10 mm. These compositions were found to be more viscous and to have a better viscosity index than the original fluorocarbon oils, as shown in the following Table II, whereby the value of the fluorocarbon oils as lubricants was greatly increased:

Table II

Distilling Range Fluorocarbon Oil	Interpolymer, Per Cent	Viscosity (centistokes)		Viscosity Index
		100° F.	210° F.	
130–150° C./10 mm		37.4	2.8	−676
130–150° C./10 mm	0.5	46.7	3.5	−488
130–150° C./10 mm	1.0	159.6	14.3	+100
130–150° C./10 mm	2.0	1205.		
150–170° C./10 mm		169.	5.05	−968
150–170° C./10 mm	0.5	184.	5.7	−674
150–170° C./10 mm	2.0	30,300.		

EXAMPLE 4

9 grams of fluorocarbon oil (distilling range 210° C. to 240° C. at 10 mm.) and 1 g. of an interpolymer powder (70% tetrafluoroethylene and 30% chlorotrifluoroethylene) were heated to about 240° C. (the transition point) where the mixture changed from a thin slurry to a very viscous irreversible mass or grease. The product was useful as a lubricant under corrosive conditions.

EXAMPLE 5

16 parts of an interpolymer (70% tetrafluoroethylene and 30% chlorotrifluoroethylene), in powder form, and 84 parts of fluorocarbon oil (distilling range 130–300° C./10 mm.) were treated as in Example 4 to produce a grease.

EXAMPLE 6

One gram of interpolymer (79% tetrafluoroethylene and 21% chlorotrifluoroethylene), in powder form, has heated with 10 g. of fluorocarbon oil (distilling range 130–250° C./10 mm.). At 150° C., the polymer began to swell. At 190–200° C., almost all of the fluorocarbon oil appeared to be absorbed by the polymer, but the polymer particles were not fused together. At 280° C., the entire mass became homogeneous, viscous and clear. When cooled and put through a muller, a grease of good consistency was obtained. Such grease was extremely valuable as a lubricant for valves and plug-cocks in use under corrosive conditions.

EXAMPLE 7

One gram of interpolymer (90% tetrafluoroethylene and 10% chlorotrifluoroethylene), in powder form, was heated with 9 g. of fluorocarbon oil (distilling range 130–300° C./10 mm.). At 320° C., the mass suddenly became clear, homogeneous and viscous. It was then cooled and mulled. The product was a good grease.

EXAMPLE 8

One gram of interpolymer (98.5% tetrafluoroethylene and 1.5% chlorotrifluoroethylene), in powder form, was heated with 10 g. of fluorocarbon oil (distilling range 130–250° C./10 mm.). The transition, from a slurry of interpolymer in fluorocarbon oil to a homogeneous, viscous, clear mass, occurred at 335° C. This material, when worked up as in Example 6, had a good greasy consistency. It was valuable as a lubricant under extremely corrosive conditions. It has an advantage over the grease of Example 6 in that it can be used under higher temperature conditions because of its higher transition temperature.

EXAMPLE 9

About 1 g. of an interpolymer (20% tetrafluoroethylene and 80% chlorotrifluoroethylene), in powder form, and 10 g. of fluorocarbon oil (distilling range 130–250° C./10 mm.) were heated together as in Example 6. At 175° C., there was a partial transition to produce a translucent oil composed of the major proportion of the interpolymer and the fluorocarbon oil and, admixed therewith, a small proportion of the interpolymer in the form of hard particles of about the size of grains of sand. Upon heating to 330° C., the particles fused into a single lump and the oil phase became slightly more cloudy. After cooling

and mulling in the usual manner, a satisfactory grease was obtained. All, except a very small proportion, of the particles and fused lump of the interpolymer could be mulled into the grease but with some difficulty.

EXAMPLE 10

About 1 g. of interpolymer (8% tetrafluoroethylene and 92% chlorotrifluoroethylene), in powder form, and 9 g. of fluorocarbon oil (distilling range 130–250° C./10 mm.) were heated together as in Example 6. At 190° C., the interpolymer melted but there was no transition point as in the previous examples, nor was a homogeneous mass obtained even when heated to 340° C. Upon cooling, there was obtained chunks of fused hard plasticized polymer and uncombined fluorocarbon oil which could be readily separated by decantation or filtration and could not be mulled to form a grease.

EXAMPLE 11

One gram of interpolymer (99% tetrafluoroethylene and 1% chlorotrifluoroethylene), in powder form, was heated with 10 g. of fluorocarbon oil (distilling range 130–250° C./10 mm.) as in Example 6. At 180° C., the interpolymer coagulated to some extent, but no other change was noted up to a temperature of 340° C. (the boiling point of the fluorocarbon oil). After cooling, it was found that the mass was a mixture of hard particles of fused plasticized interpolymer and uncombined oil which could be readily separated, and the particles could not be broken up in a muller.

Examples 10 and 11 have been included for purposes of comparison and particularly to illustrate the critical nature of the limits of interpolymer composition.

It will be understood that the foregoing examples have been given for illustrative purposes solely and that my invention is not to be limited to the specific embodiments disclosed therein. It will be readily understood by those skilled in the art that variations may be made in the composition of the interpolymer, the fluorocarbon oil, the proportions of interpolymer to fluorocarbon oil, and in the conditions of preparing my compositions, within the limits hereinbefore set forth.

From the preceding description and the examples, it will be apparent that, by my invention, it is possible to convert the fluorocarbon oils to thickened oils and greases having improved properties whereby the compositions of my invention have increased utility and, particularly, are useful for many purposes of which the interpolymers and the fluorocarbon oils are inapplicable. The thickened oils and greases have the advantage over the thickened hydrocarbon oils and hydrocarbon greases in that they are useful under conditions, such as in the presence of highly corrosive and reactive chemicals and elevated temperatures, where the hydrocarbon oils and greases are not suitable. It is thus apparent that my invention constitutes a valuable and important advance in the art.

This is a continuation-in-part of my application Serial No. 51,183 filed September 25, 1948, now abandoned.

I claim:

1. A composition which is a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 50° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 98.5% to about 20% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 0.5% to about 20% by weight of the composition; such composition being stable and homogeneous in appearance, having a consistency in the range of thickened oils and greases at atmospheric temperatures, and being capable of being heated to temperatures between 175° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

2. A composition which is a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 98.5% to about 20% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 0.5% to about 20% by weight of the composition; such composition being stable and homogeneous in appearance, having a consistency in the range of thickened oils and greases at atmospheric temperatures, and being capable of being heated to temperatures between 175° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

3. A composition which is a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 50° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 90% to about 34% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 0.5% to about 20% by weight of the composition; such composition being stable and homogeneous in appearance, having a consistency in the range of thickened oils and greases at atmospheric temperatures, and being capable of being heated to temperatures between 181° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

4. A composition which is a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 90% to about 34% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 0.5% to about 20% by weight of the composition; such composition being stable and homogeneous in appearance, having a consistency in the range of thickened oils and greases at atmospheric temperatures, and being capable of being heated to temperatures between 181° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

5. A composition which is substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetra-

fluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 90% to about 57% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 0.5% to about 20% by weight of the composition; such composition being stable and homogeneous in appearance, having a consistency in the range of thickened oils and greases at atmospheric temperatures, and being capable of being heated to temperatures between 200° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

6. A composition which is a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 98.5% to about 20% by weight, the interpolymer being in the form of stringy masses and constituting from about 2% to about 20% by weight of the composition; such composition being stable and homogeneous in appearance, having the consistency of a grease at atmospheric temperatures, and being capable of being heated to temperatures between 175° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

7. A composition which is substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 90% to about 34% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 2% to about 20% by weight of the composition; such composition being stable and homogeneous in appearance, having the consistency of a grease at atmospheric temperatures, and being capable of being heated to temperatures between 181° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

8. A composition which is a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 90% to about 57% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 2% to about 20% by weight of the composition; such composition being stable and homogeneous in appearance, having the consistency of a grease at atmospheric temperatures, and being capable of being heated to temperatures between 200° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

9. A composition which is a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 50° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 98.5% to about 20% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 0.5% to about 2% by weight of the composition; such composition being stable and homogeneous in appearance, having a consistency in the range of thickened oils at atmospheric temperatures, and being capable of being heated to temperatures between 175° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

10. A composition which is a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure having incorporated therein an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene in which the tetrafluoroethylene is in the proportion of from about 90% to about 57% by weight, the interpolymer being in the form of stringy fibrous masses and constituting from about 0.5% to about 2% by weight of the composition; such composition being stable and homogeneous in appearance, having a consistency in the range of thickened oils at atmospheric temperatures, and being capable of being heated to temperatures between 200° C. and 400° C. where it forms a clear liquid and then cooled to atmospheric temperatures and to its original condition.

11. The process for preparing compositions of the character of thickened oils and greases which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 98.5% to about 20% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 50° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 0.5% to about 20% by weight of the mixture, heating the mixture to a temperature of from about 175° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

12. The process for preparaing compositions of the character of thickened oils and greases which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 98.5% to about 20% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 0.5% to about 20% by weight of the mixture, heating the mixture to a temperature of from about 175° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

13. The process for preparing compositions of the character of thickened oils and greases which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 90% to about 34% by weight, with

a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 50° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 0.5% to about 20% by weight of the mixture, heating the mixture to a temperature of from about 181° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

14. The process for preparing compositions of the character of thickened oils and greases which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 90% to about 34% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 0.5% to about 20% by weight of the mixture, heating the mixture to a temperature of from about 181° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

15. The process for preparing compositions of the character of thickened oils and greases which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 90% to about 57% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 0.5% to about 20% by weight of the mixture, heating the mixture to a temperature of from about 200° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

16. The process for preparing compositions of the character of greases which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 98.5% to about 20% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 2% to about 20% by weight of the mixture, heating the mixture to a temperature of from about 175° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

17. The process for preparing compositions of the character of greases which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 90% to about 34% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 2% to about 20% by weight of the mixture, heating the mixture to a temperature of from about 181° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

18. The process for preparing compositions of the character of greases which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 90% to about 57% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 2% to about 20% by weight of the mixture, heating the mixture to a temperature of from about 200° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

19. The process for preparing compositions of the character of thickened oils which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 98.5% to about 20% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 50° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 0.5% to about 2% by weight of the mixture, heating the mixture to a temperature of from about 175° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

20. The process for preparing compositions of the character of thickened oils which comprises mixing an interpolymer of tetrafluoroethylene and chlorotrifluoroethylene, in which the tetrafluoroethylene is in the proportion of from about 90% to about 57% by weight, with a substantially completely fluorinated hydrocarbon oil distilling at temperatures in the range of from about 130° C. to about 300° C. at 10 mm. Hg pressure, the proportions being such that the interpolymer constitutes from about 0.5% to about 2% by weight of the mixture, heating the mixture to a temperature of from about 200° C. to 400° C. and to at least the transition temperature which corresponds substantially to that indicated by the curve on the accompanying drawing for the

interpolymer employed, maintaining the mixture at such temperature until it becomes clear and homogeneous in appearance and more viscous, and then cooling.

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