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経済産業省 貿易経済協力局 貿易管理部

安全保障貿易管理課 浅井課長殿

安全保障貿易審査課 横田課長殿

(写) 安全保障貿易管理政策課 熊野分析官殿

(写) 安全保障貿易管理課 井口課長補佐殿、斎藤課長補佐殿

(写) 安全保障貿易管理課 相部課長補佐殿

(写) 安全保障貿易審査課 菊島総括課長補佐殿

一般財団法人 安全保障貿易情報センター

素材専門委員会

先端材料関連分科会

主査 宮寄 斉

貨物等省令第4条第十一号の改正要望

表題の件につきまして、下記のとおり要望いたしますので、何卒ご検討いただきますようよろしくお願いいたします。

記

1. 要望内容

貨物等省令第4条第十一号の改正を、以下の通り要望します。

(1) 改正案の要旨

同号ハ(二)ポリクロロトリフルオロエチレンに「油状又はワックス状の改質品に限る。」のかっこ書きを追加する。

(2) 改正案（太字下線部が改正提案部分）

第4条第十一号

潤滑剤として使用することができる材料、振動防止用に使用することができる液体又は冷媒用の液体であって、次のいずれかに該当するもの

イ 削除

ロ (略)

ハ 振動防止用に使用することができる液体であって、純度が99.8パーセントを超え、かつ、径が200マイクロメートル以上の粒状の不純物の数が100ミリリットル当たり25個未満のもののうち、次のいずれかに該当する物質の重量が全重量の85パーセント以上のもの

(一) ジブロモテトラフルオロエタン

(二) ポリクロロトリフルオロエチレン（油状又はワックス状の改質品に限る。）

(三) ポリブロモトリフルオロエチレン

(以下略)

(3) 現法令

第4条第十一号

潤滑剤として使用することができる材料、振動防止用に使用することができる液体又は冷

媒用の液体であって、次のいずれかに該当するもの

- イ 削除
- ロ (略)
- ハ 振動防止用に使用することができる液体であって、純度が 99.8 パーセントを超え、かつ、径が 200 マイクロメートル以上の粒状の不純物の数が 100 ミリリットル当たり 25 個未満のもののうち、次のいずれかに該当する物質の重量が全重量の 85 パーセント以上のもの
 - (一) ジブロモテトラフルオロエタン
 - (二) ポリクロロトリフルオロエチレン
 - (三) ポリブロモトリフルオロエチレン(以下略)

2. 要望の背景・理由等

本要望は貨物等省令第4条第十一号ハ(二)と Wassenaar Arrangement(WA)の原文との一致を提案するものです。

(1) 貨物等省令第4条第十一号ハ(二)とWA原文との比較

- 1) 本要望に係る貨物等省令第4条第十一号ハ(二)と対応するWA原文の1.C.6.c.3.b.の関係は以下の通りです。
 - ・WA原文1.C.6.c.3.b.で規制される Polychlorotrifluoroethylene においては、(oily and waxy modifications only)のかっこ書きがあり、同項番では「(油状又はワックス状の改質されたものに限る。)(日本語訳)」が規定されています(以下のWA原文中の太字下線部分ご参照下さい)。
 - ・一方、貨物等省令第4条第十一号ハ(二)の条文では「ポリクロロトリフルオロエチレン」のみが記載されており、(oily and waxy modifications only)に相当する内容が反映されていません。
- 2) 従いまして、対応する国内法令である貨物等省令第4条第十一号ハ(二)のポリクロロトリフルオロエチレンに、上記WA1.C.6.c.3b.で規定される(oily and waxy modifications only)を反映することを要望いたします。
- 3) なお、WA原文中の"modifications"を「改質」と訳する点につきまして、WAの他項番2.B.5.(a)、2.E.3.f.及び、その関連 *Technical Notes* において"surface modifications"という語句が使用されております。これに対し、我が国、輸出令別表第1の6の項(5)、貨物等省令第5条第七号の「運用通達における解釈を要する語」中で「表面改質」という訳語が使用されております(添付資料1ご参照下さい)。

【ご参考】

対応するWA原文(太字下線部が本要望に係る箇所になります)

1. C. 6. Fluids and lubricating materials, as follows:
 - a. Not used since 2015
 - b. (略)
 - c. Damping or flotation fluids having all of the following
 1. Purity exceeding 99.8%;
 2. Containing less than 25 particles of 200 µm or larger in size per 100 ml; and
 3. Made from at least 85% of any of the following:
 - a. Dibromotetrafluoroethane (CAS 25497-30-7, 124-73-2, 27336-23-8);
 - b. Polychlorotrifluoroethylene (**oily and waxy modifications only**); or
- (以下略)

(2) WA1.C.6.c.3.b.の規制理由と我が国産業界における当該貨物に係る現状

1) 本項番に係る「油状又はワックス状」のポリクロロトリフルオロエチレン（以後「PCTFE」といいます。）を、規制対象である振動防止用液体として使用するための具体的な改質方法は、例えば、米国特許（添付資料2、3及び4）に開示されています。以下に例示します。

①別の（比重の高い）液体を混合し、比重を高くする（添付2；米国特許2992991号）

②数種類のワックス状のPCTFEを有機溶媒に溶かして濾過することによって超高分子成分を取り除き、その後溶媒を除去することにより、高温において均質な液体となるワックスを調製する（添付3及び4；米国特許3076765号）

これら手法によって改質されたPCTFEがWA項番1.C.6.c.3.b.で規制される対象貨物であると思料します。

2) 例えば米国商務省（BIS）は、PCTFEを成分とするものの改質されていない、すなわち未改質PCTFE製品（例えば、製品名Halocarbon Oil、米国Halocarbon社製）を非該当品（米国輸出規制EAR99、添付資料5参照）と認定し、当該の未改質PCTFEは海外で流通しています。

3) 一方、我が国では、未改質PCTFEを成分とする貨物は、貨物等省令第4条十一号ハ（二）の規定に従い、リスト規制品として扱っております。

4) 未改質PCTFEを成分とする具体的製品としては、酸素用ポンプ潤滑剤に用いられるふっ素オイル（商品名ダイフロイル；ダイキン工業株式会社製）が例示でき、国内製造・販売されるほか、リスト規制品として輸出されております（上記のような改質が行われていないため、貨物等省令第4条第十一号で規制対象となる振動防止用途での使用は難しいと考えられ、実際に引き合いや販売実績はありません）。この製品は、製造者が直接海外に輸出する以外にも、メンテナンス用途等で国内の購入機会も多いと考えられ、多くの顧客でリスト規制品として、特に厳格な管理を行っている現状です。

以上より、本要望は国際レジーム（WA）と我が国法令（貨物等省令）のハーモナイズの観点から、WA1.C.6.c.3.b.で規制されるPolychlorotrifluoroethyleneと、貨物等省令第4条十一号ハ（二）のポリクロロトリフルオロエチレンの規制内容を一致させ、同号で規定される対象貨物の明確化を目的とするものです。

これにより製造者、輸出者及びその他関係者が、法令に定める規制趣旨を適正に運用することが可能となり、以てより適正な輸出管理の実現につながるものと思料します。

【添付資料】

- ・添付資料1 "surface modification"を「表面改質」と訳したWA原文と貨物等省令の対比
- ・添付資料2 ポリクロロトリフルオロエチレン改質に関する米国特許2992991号 英文明細書
- ・添付資料3 ポリクロロトリフルオロエチレン改質に関する米国特許3076765号 和文抄録
- ・添付資料4 ポリクロロトリフルオロエチレン改質に関する米国特許3076765号 英文明細書
- ・添付資料5 未改質ポリクロロトリフルオロエチレンをEAR99とするBIS見解書

以上

添付資料1

"surface modification"を「表面改質」と訳した WA 原文と貨物等省令の対比

<p>WA 原文 CATEGORY 2 <u>TABLE - DEPOSITION TECHNIQUES - TECHNICAL NOTE</u></p>	<p>貨物等省令：第5条第七号 (運用通達における解釈を要する語)</p>
<p>a. Chemical Vapor Deposition (CVD) is an overlay coating or surface modification coating process wherein a metal, alloy, “composite”, dielectric or ceramic is deposited upon a heated substrate. Gaseous reactants are decomposed or combined in the vicinity of a substrate resulting in the deposition of the desired elemental, alloy or compound material on the substrate. Energy for this decomposition or chemical reaction process may be provided by the heat of the substrate, a glow discharge plasma, or “laser” irradiation.</p>	<p>『原料ガスの化学反応により生成するコーティング材料を基材の表面に定着させる方法』 加熱した基材の上に金属、合金、複合材料、誘導体又はセラミックを、上塗り又は表面改質のために被覆するプロセスをいう。気体状の反応物が基材近傍で分解、結合することによって、目的の元素、合金又は化合物が基材上に被覆される。分解若しくは化学反応プロセスの駆動エネルギーは、基材の熱、プラズマからの放電又はレーザーの照射から得られる。</p>
<p>g. Ion Implantation is a surface modification coating process in which the element to be alloyed is ionized, accelerated through a potential gradient and implanted into the surface region of the substrate.</p>	<p>『イオン注入法』 合金化すべき元素がイオン化され、電界により加速されて基材の表面部分に打ち込まれることによって表面改質被覆を行うプロセスをいう。</p>

United States Patent Office

2,992,991
Patented July 18, 1961

1

2,992,991

THERMALLY STABLE VISCOUS COMPOSITION CONTAINING A CHLORFLUORINATED ALKANE OIL

Fred W. West, Paterson, N.J., assignor, by mesne assignments, to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware
No Drawing. Filed Mar. 26, 1957, Ser. No. 648,489
10 Claims. (Cl. 252-78)

This invention relates to a high viscosity material and to the preparation thereof. In one aspect this invention relates to a flotation fluid for reducing frictional losses in instruments and machines. Another aspect of this invention relates to a damping fluid for reducing impact and vibration damage and offering viscous non-elastic restraint to moving parts within a gyro. Another aspect of this invention relates to a halogenated, viscous material having a low pour point and high shear stability. Another aspect of this invention relates to a chlorofluorinated lubricating oil having a viscosity which is substantially stable over a wide temperature range. Still another aspect of this invention relates to chlorofluorinated polymers as damping and flotation fluids for gyro mechanisms.

Gyro mechanisms which are used for missile guidance systems, aircraft navigation instruments, fire control systems and navigation instruments on ships have now achieved wide recognition. For some of the improved gyros now being designed there exists a need for a highly viscous, high density material which has a low pour point and which is stable at high temperatures, that is, at temperatures of about 200° F. A gyro in a guided missile, for example, in responding to change in speed, direction and attitude may provide the only stable reference with respect to the earth by which the missile can be navigated. The precision required in the control of high speed, long range missile and aircraft has placed new demands upon gyros. To meet these demands a relatively new gyro has been designed which requires a suitable fluid to buoy the gyro float. Various fluids and waxes have been employed for this purpose but these have not been able to meet the requirements demanded for a material of this type. Typical specifications for a gyro fluid which is used to float the gyro in an integrating machine are presented in Table I.

TABLE I

Temperature Class, ° F.	Viscosity, cp.	Density, g./cc.	Cloud Point, ° F.
120.....	3,000	1.958	less than 115.
140.....	¹ 2,800	1.949	less than 135.
160.....	600	1.922	less than 155.
160.....	1,000	1.928	Do.
160.....	2,000	¹ 1.930	Do.

¹ Greater than.

In other cases, where the restraint to precision in the gyro is supplied by resilient member and where the fluid is not required to float the gyro, the viscosity requirements are much lower than those recorded above in Table I. For example, a viscosity of between about 100 and about

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1,000 centipoise at 100° F., may be required. One specification requires a viscosity within this range and a density of about 1.8 at 100° F. Additional desirable characteristics of some of these gyro fluids which has heretofore been unattainable is that they remain liquid at low temperatures, have cloud points not above room temperature while, at the same time, maintain suitable densities and viscosities. Some gyros now in design have small float apparent densities and although a high viscosity is needed, the density may be as low as 1.78 or lower. Thus, it is observed that requirements for gyro fluids may vary considerably depending upon the particular mechanism in which the fluid is to be employed.

Other instruments such as bi-metallic dial type thermometers and chemical seal pulsation dampeners have also indicated a need for a highly viscous material which meets many of the specifications mentioned above.

It is, therefore, an object of the present invention to provide a material having a high viscosity, a low clear point and a low pour point and to provide a method for the preparation thereof.

Another object of this invention is to provide a non-corrosive, thermally stable chlorofluorinated alkane solution suitable for use as a damping and flotation fluid.

Another object of this invention is to provide a chlorofluorinated alkane solution which remains clear at room temperature.

Another object is to provide a fluid containing a polymer of chlorotrifluoroethylene having a viscosity of about 600 centipoise or higher at 140° F., which fluid is essentially non-volatile at temperatures as high as 200° F.

Another object is to provide a polymeric mixture of chlorotrifluoroethylene suitable for use as a damping and flotation fluid in a gyroscope.

Still another object of this invention is to provide a commercially feasible method for the preparation of a chlorofluorinated alkane solution for use as a damping and flotation fluid having the above valuable properties.

Other objects and advantages of the present invention will become apparent to those skilled in the art from the accompanying description and disclosure.

According to this invention a compatible normally solid polymer, such as for example, chlorotrifluoroethylene and vinylidene fluoride copolymer having a specific gravity (Jolly balance) at 75° F. of about 2.02 and a dilute solution viscosity (DSV) of between about 0.5 and about 2.0 at 266° F. is admixed with and dissolved in a chlorofluorinated alkane oil, for example, a polychlorotrifluoroethylene oil. The normally solid polymer and the chlorofluorinated alkane oil are intimately mixed at a temperature between about 20° C. and about 200° C. or higher until a homogeneous solution having a constant viscosity is obtained and the resulting product is a viscous oil having a low pour point, low volatility and high density.

The dilute solution viscosity (DSV) of the normally solid polymer is determined by dissolving a sample of the polymer in dichlorobenzotrifluoride to a concentration of 0.75 weight percent solvent. The sample is mixed with the dichlorobenzotrifluoride in a flask which is placed in a bath at 300° F. and stirred for 3 to 4 hours or until the sample is completely dissolved. The resulting solution is removed from the flask and poured into a modified Ubbelohde viscosimeter equipped with a sinter disk

through which the solution is filtered. The viscosimeter is maintained at 266° F. by means of a thermostatically controlled bath. The liquid is drawn up through a graduated, calibrated capillary of the viscosity tube and the time it requires for the liquid to descend from one point in the graduated capillary to another is recorded in seconds. This value is multiplied by the factor of the tube to obtain a value in centistokes. This method of measuring viscosity has been applied to solid polymers having dilute solution viscosities between about 0.5 and about 3 or higher when the polymer is soluble in the solvent at the given temperature.

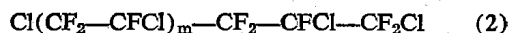
The chlorofluorinated alkane oil, or major component, of the present invention is an alkane having a minimum density of about 1.7 grams/cc. at 140° F. and containing between 4 and 22 carbon atoms per molecule. The oil is preferably a perchlorofluorinated alkane oil which includes the homopolymer of chlorotrifluoroethylene having a viscosity at 210° F. of between about 1 and about 40 centistokes and a molecular weight of between about 300 and about 1,000 as the most preferred member of this group. Polychlorotrifluoroethylene oils having these properties are represented by the following general formula



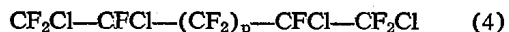
wherein x is an integer between 3 and 9 and Y and Z are normally gaseous halogen atoms (fluorine and chlorine atoms) or a moiety derived from an alkyl telogen which is completely halogenated with normally gaseous halogen atoms. The preparation of polychlorotrifluoroethylene oils wherein Y and Z are normally gaseous halogen atoms is given in U.S. Patent 2,770,659. The polychlorotrifluoroethylenes wherein Y and Z are chlorine atoms are prepared by the telomerization of chlorotrifluoroethylene with sulfuryl chloride and are commercially available as Kel-F #1 Oil, which is a mixture of polychlorotrifluoroethylenes having a molecular weight between about 300 and about 500, Kel-F #3 Oil, which is a mixture of polychlorotrifluoroethylenes having a molecular weight between about 500 and about 780 and Kel-F #10 Oil, which is a mixture of polychlorotrifluoroethylenes having a molecular weight between about 780 and about 1,000. The individual oils can be employed separately or any combination of them can be employed and used as the major component.

The preparation of other perchlorotrifluoroethylene oils in this most preferred group wherein Y and Z are moieties derived from an alkyl telogen which is completely halogenated with normally gaseous halogen atoms, such as, for example, chlorotrifluoromethane, trichlorotrifluoroethane, pentachlorotrifluoropropane, etc., is set forth in copending applications of William S. Barnhart, Serial No. 347,186 (filed April 6, 1953), now U.S. 2,875,252, and Serial No. 452,708 (filed August 27, 1954), now abandoned.

Other preferred perchlorofluorinated alkane oils which are useful in the present invention include the following:

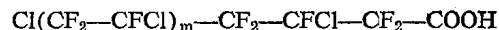


and



wherein m is an integer between 1 and 9; n is an integer between 2 and 20 and p is an integer between 0 and 18. These perchlorofluorinated alkane oils are obtained from the chlorination of perchlorofluorochlorinated olefins to yield compounds corresponding to Formula 2, and from the chlorination of perfluorinated olefins to yield compounds corresponding to Formulae 3 and 4. The chlorination is carried out with molecular chlorine at a temperature between about 20° C. and about 150° C. for a period of from about 0.5 to about 24 hours. The perchlorofluorinated olefin $Cl(CF_2-CFCl)_m-CF_2-CF=CF_2$,

can be derived from the decarboxylation of the perchlorofluoromonocarboxylic acid,



wherein m is an integer between 2 and 9. The decarboxylation is described in U.S. application Serial No. 517,926 filed June 24, 1955, in the names of William S. Barnhart and Robert H. Wade. This olefin can also be prepared by chlorinating the diolefin obtained from the thermal cracking of polychlorotrifluoroethylene at a temperature between about 100° C. and about 500° C. in the presence of steam. In addition to the diolefin obtained from the pyrolysis of polychlorotrifluoroethylene, the monoolefin $CF_2=CF-(CF_2-CFCl)_x$ wherein x is an integer between 2 and 9, is also produced. This monoolefin upon chlorination yields compounds corresponding to the perchlorofluorinated compound of Formula 1. Each of the foregoing perchlorofluorinated alkanes may be employed individually or any mixture of the foregoing perchlorofluorinated alkanes may be used as the major component of the present invention.

Some specific examples of the preferred perchlorofluorinated alkane oils which correspond to Formulae 2, 3, and 4 above are:

1,2,4,6,8,9-hexachlorotetradecafluorononane,
1,2,4,6,8,10,11-heptachloroheptadecafluorohendecane,
1,2,4,6,7-pentachloroundecafluoroheptane,
1,2,4,6,8,10,12,14,15-nonachloroperfluoropentadecane,
1,2-dichlorohexadecafluorooctane,
1,2-dichlorooctadecafluorononane,
1,2-dichloroperfluorooctadecane,
1,2-dichloroperfluoroicosane,
1,2,5,6-tetrachlorodecafluorohexane,
1,2,9,10-tetrachlorooctadecafluorodecane,
1,2,13,14-tetrachloroperfluorotetradecane,
1,2,6,7-tetrachlorohexadecafluorononane,
1,2,3,4-tetrachlorohexafluorobutane, and
1,2-dichlorodecafluoropentane.

Examples of other preferred perchlorofluorinated alkane oils are:

1,2,3,6,7,8-hexachlorododecafluorooctane,
1-chloroperfluorooctane,
1-chloroperfluorodecane,
3,4-dichloroperfluorohexane,
2,3,3,4,4,5-hexachlorooctafluorohexane,
1,1,2,3,4,4-hexachloro-2,3-bis(trifluoromethyl)butane,
2,5-dichloroperfluorohexane,
2,4-dichloro-2-(trifluoromethyl)methyl pentane, and
2,3-dichloro-2,3-bis(trifluoromethyl)butane.

Other chlorofluorinated alkane oils which are suitably used in the process of the present invention are the aliphatic alkane oils which are more than half halogenated. This group includes chlorofluorinated oils prepared by the hydrochlorination of any of the previously mentioned olefins with hydrogen chloride at a temperature between about 50° C. and about 300° C. The compounds formed by the addition of hydrogen chloride to the above mentioned olefins are β -hydrochlorofluorinated alkanes.

Specific examples of some of these alkanes are:

β -hydro-1,4,5-trichlorooctafluoropentane,
 β -hydro-1,4,6,8,9-pentachlorotetradecafluorononane,
 β -hydro-1-chlorooctafluorobutane,
 β -hydro-1-chlorododecafluorohexane,
 β -hydro-1-chloroperfluorodecane,
2,8-dihydro-1,9-dichlorohexadecafluorononane,
2,3-dihydro-1,4-dichlorohexafluorobutane,
2,4-dihydro-1,5-dichlorooctafluoropentane, and
2,5-dihydro-1,6-dichlorodecafluorohexane.

Still other chlorofluorinated alkane oils employed as the major component in the fluids of the present invention

include the copolymeric oils of chlorotrifluoroethylene and other halogenated aliphatic olefin comonomers, such as, for example, vinylidene fluoride, vinyl fluoride, 1-chloro-1-fluoroethylene, trifluoroethylene, vinylidene chloride and dichlorohexafluorobutene. Of these copolymeric oils the chlorotrifluoroethylene and vinylidene fluoride copolymer is preferred.

The normally solid polymers of the present invention are those which are compatible with the chlorofluorinated alkane oils and which have a DSV between about 0.2 and about 3. The preferred normally solid polymer, or viscosity improver, which is admixed with the chlorofluorinated alkane is the copolymer of chlorotrifluoroethylene and vinylidene fluoride which has a specific gravity at 75° F. of between about 2.0 and about 2.2, a DSV between about 0.5 and about 2.0 at 266° F. and which contains between about 10 mol percent and about 50 mol percent vinylidene fluoride, most preferably between about 15 mol percent and about 35 mol percent vinylidene fluoride. The thermoplastic resin containing between about 15 mol percent and about 35 mol percent vinylidene fluoride is commercially available as Kel-F 800 Resin and its method of preparation is described in U.S. Patent 2,752,332.

Other viscosity improvers which are suitably admixed with the chlorofluorinated alkane oils and which have a DSV at 266° F. of between about 0.2 and about 3 are solid polymers which have a minimum density of about 0.9 at 100° F. Examples of some of these solid polymers are the silicon rubber gums, polymethacrylate, polyvinyl chloride, polystyrene, polydichlorostyrene, polybutene, vinyl chloride and vinylacetate copolymer, vinyl chloride and acrylonitrile copolymer, chlorinated rubbers, ethyl cellulose polymer, cellulose acetate, butyrate polymer, cellulose nitrate polymer and vinyl butyral polymer.

Generally, for good results and ease of mixing, the normally solid polymer should be finely divided. For example, in the case of Kel-F 800 Resin, a particle size below about 250 microns is suitable; however, a particle size which will pass 90 percent through a 100 or higher mesh screen (U.S. Bureau Standards, standard screen series) is preferred.

In accordance with this invention the normally solid polymer is preferably added to the chlorofluorinated alkane oil in an amount between about 2 and about 30 weight percent of the normally solid polymer. The amount of normally solid polymer added to the oil is dependent upon the initial viscosity of the oil and the viscosity required for the end use. Generally, when employing Kel-F #1 Oil up to 30 weight percent of the normally solid polymer may be added; when using Kel-F #3 Oil, it is usually necessary to add an amount above about 20 weight percent of the normally solid polymer. When Kel-F #10 Oil is used, the normally solid polymer is added in an amount which generally varies between about 2.5 and about 15 weight percent of normally solid polymer.

In carrying out the process of the present invention under preferred conditions, the normally solid polymer is added to the chlorofluorinated alkane oil at a temperature between about 100° C. and about 125° C., although, a temperature between about 20° C. and about 250° C. is satisfactory and may be used if desired. The mixture is agitated vigorously for a period of from about 1 to about 100 hours or until a homogeneous solution and a constant viscosity is obtained. To insure the complete homogeneity of the solution, the resulting solution can be filtered to remove any gel-like particles which may be formed in the solution. The filtration step is usually omitted when the solution has achieved complete homogeneity upon being mixed for a sufficient period of time.

Although it is preferable and less time consuming in the mixing of ingredients to add the normally solid polymer to the chlorofluorinated oil, it is also within the scope of the present invention to add the oil to the solid

polymer. This is accomplished by mixing a small amount of oil with the solid polymer so as to moisten the particles and then adding the remaining portion of oil to the moistened solid polymer. Generally, this procedure requires a longer period of time with agitation to arrive at a substantially homogeneous solution; for example, a period between about 10 to about 200 hours.

If several concentrations of normally solid polymer are to be prepared in the same chlorofluorinated alkane oil, it is often convenient to prepare a stock solution of the same or of higher normally solid polymer concentration than is required by the most concentrated of the homogeneous solutions desired. To obtain the homogeneous solutions having a lower normally solid polymer concentration, the stock solution or a portion of the stock solution is then diluted accordingly until the required concentration is attained.

The reaction may be carried out in any suitable reactor such as, for example, an open glass flask, a metal reactor, a thermostatically controlled container equipped with a reflux condenser. When using one of the more volatile major components, such as, for example, Kel-F #1 Oil, a reflux condenser is generally employed so that light ends escaping from the solution are returned to the system.

In certain cases, where a high density major component, for example, Kel-F #10 Oil is mixed with a normally solid polymer having high density, the specifications for a particular gyro fluid may require lower density. In these instances a cosolvent such as a hydrocarbon ester containing between about 10 and about 30 carbon atoms can be added to the chlorofluorinated oil before mixing with the solid polymer or the cosolvent can be added to the homogeneous solution after mixing has been accomplished. Examples of such ester additives are dioctylphthalate, di(2-ethylhexyl)phthalate, dioctylazelate, didecylazelate, dihexylsebacate, dibutylglutarate and dioctylsuccinate. When used, these additives are added in an amount between about 0.5 weight percent and about 50 weight percent, preferably 1 weight percent and about 15 weight percent based on the weight of the fluid components.

In other cases the homogeneous solution obtained from the mixing of the chlorofluorinated oil and the normally solid polymer is used directly as a high viscosity fluid in gyro mechanisms and is generally introduced into the gyroscope cavity under vacuum.

The following examples are offered as a better understanding of the present invention and are not to be construed as unnecessarily limiting thereto.

The properties which distinguish the Kel-F Oils #1, 3 and 10 are given below in Table II.

TABLE II

	Kel-F Oil #1	Kel-F Oil #3	Kel-F Oil #10
Refractive Index, n_D at 77° F.	1.401	1.405	1.410
Viscosity in cs.:			
100° F.	3	25	220
210° F.	1	3	10
Viscosity in cp., 100° F.	5.6	47	425
Pour Point, ° F.	-70	-45	-30
Heat of Vaporization, K calories per mol.	10.7	14.5	17.1

All of the homogeneous solutions in the following Table III, Examples 1 through 11, had clear points below room temperature (20° C.). These homogeneous solutions were prepared by adding Kel-F 800 Resin (DSV 0.5) to Kel-F Oil in a glass flask equipped with a thermometer and a Hershberg stirrer at a temperature of between about 110° C. and about 120° C. The solution was vigorously stirred for a period of about 30 hours after which a completely homogeneous solution and a constant viscosity was obtained.

TABLE III
HOMOGENEOUS SOLUTIONS OF KEL-F 800 RESIN IN KEL-F OILS

Example No.	Kel-F 800 Resin, Weight Percent	Kel-F Oil No.	Viscosity in cs.		Density in g./cc.		Pour Point, ° F.	Volatility, Percent at 311° F.	Viscosity in cp.		
			140° F.	210° F.	140° F.	210° F.			140° F.	210° F.	68° F.
1	2.5	1	9.41	4.23	1.7886	1.7229	1-80	-----	18.81	7.29	60.3
2	5.0	1	38.4	13.97	1.7907	1.7254	1-80	-----	68.6	24.5	298.5
3	7.5	1	144	45.1	1.7958	1.7290	-50	60.18	258.5	77.9	1,935
4	10.0	1	318.9	89.87	1.8033	1.7390	-----	-----	575	156.3	-----
5	2.5	3	72.9	15.9	1.8698	1.8095	-20	25.3	136	28.8	-----
6	5.0	3	325	61.3	1.8728	1.8121	10	25.7	609	111.2	-----
7	7.5	3	1,171	191.3	1.8753	1.8161	35	24.9	2,196	347	-----
8	10.0	3	4,200.5	540.2	1.8799	1.8207	70	21.3	7,896	983.5	-----
9	2.5	10	372	49.3	1.908	1.851	45	6.93	710	91.3	-----
10	5.0	10	1,751	185.4	1.9099	1.852	50	6.26	3,344	343	-----
11	10.0	10	-----	1,373.8	1.9138	1.8565	85	7.31	50,000	2,550	-----

¹ Less than.

² Estimated value.

The volatility of the products in Table III above was determined by nitrogen-jet evaporation. This method

certies of homogeneous solutions prepared by mixing Kel-F 800 Resin with a perchlorofluorinated alkane oil.

TABLE IV
HOMOGENEOUS SOLUTIONS OF KEL-F 800 RESIN IN 1,1,3,5,6-PENTACHLORONONA-FLUOROHEXANE

Example No.	Kel-F 800 Resin		Viscosity in cs.		Density, grams/cc.		Pour Point, ° F.	Viscosity in cp. at 100° F.
	Wt. Percent	DSV	100° F.	210° F.	68° F.	100° F. (estimated)		
12	1.0	1.946	88.1	21.0	1.843	1.81	less than -90	158
13	1.5	1.946	159.6	37.3	1.843	1.81	less than -90	290
14	2.0	1.946	680.0	128.0	1.843	1.81	-85	1,230
15	2.0	1.946	579.0	107.0	1.843	1.81	-80	-----
16	2.0	0.56	1.99	6.0	-----	-----	less than -80	-----
17	7.5	0.56	81.6	17.7	1.850	1.82	less than -80	149
18	10.0	0.56	214.4	36.5	1.855	1.825	-60	390
19	10.0	0.56	about 390	-----	1.85	-----	-60	-----
20	1.0	1.43	27.82	7.91	1.840	-----	less than -85	50.3
21	2.0	1.43	323.35	67.45	1.843	-----	less than -80	585
22	3.0	1.43	2,135	362.0	1.847	-----	-80	3,820

HOMOGENEOUS SOLUTIONS OF KEL-F 800 RESIN IN 1,1,3,5,7,8-HEXACHLORODODECAFLUOROCTANE

23	1.0	1.946	169.9	28.8	1.898	1.87	-85	318
24	2.0	1.946	2,868.4	200.5	1.905	-----	-30	5,360
25	2.0	0.56	26.53	4.82	1.903	-----	less than -70	49.6
26	5.0	0.56	234.6	23.44	-----	1.87	-25	437

HOMOGENEOUS SOLUTIONS OF SILICONE POLYMER (DOW CORNING-CENTISTOKES AT 25° C. = 2.0) IN 1,1,3,5,7,9,11,12-OCTACHLOROPERFLUORODODECAN

	Silicone, Wt. Percent	Viscosity			Pour Point, ° F.	Density at 68° F.
		cs. at 210° F.	cs. at 100° F.	cp. at 100° F.		
27	1	6.29	104.5	198.5	40	1.932

All of the above homogeneous solutions had clear points below room temperature.

1,1,3,5,6-pentachlorononafluorohexane has a viscosity in centistokes at 100° F. of 1.87 and at 210° F. of 0.75; a density at 68° F. of 1.840; a pour point of less than -90° F. and a viscosity in centipoises at 100° F. of 3.4.

1,1,3,5,7,8-hexachlorododecafluorooctane has a viscosity in centistokes at 100° F. of 5.78 and at 210° F. of 1.45; a density at 68° F. of 1.893; a pour point of -70° F. and a viscosity in centipoises at 100° F. of 10.7.

Some other silicone polymers which may be used in place of silicone polymer from Dow Corning are the silicone rubber gums supplied by General Electric and designated as SE-76, SE-52, SE-30, SE-51, SE-33 and SE-31.

is carried out by evaporating a sample of the homogeneous solution by a stream of nitrogen preheated to 311° C. The solution is evaporated for a predetermined period of time which corresponds to the time required to evaporate 50 percent of a similar quantity of n-cetane. The volatility is expressed as percent evaporated.

The examples in the following Table IV show the prop-

All of the homogeneous solutions in the above Table IV, Examples 12 through 27, have clear points below room temperature (20° C.). These homogeneous solutions were prepared by adding the normally solid polymer to the perchlorofluorinated alkane oil at a temperature of about 100° C. The solution was vigorously agitated for a period of about 24 hours after which a

completely homogenous solution having a constant viscosity was obtained.

Example 28

This example illustrates the effect of a hydrocarbon ester when included in the homogeneous solution recipe.

Ingredients:	Weight percent
Kel-F #10 oil	89.6
Kel-F 800 Resin	6.2
Di(2-ethylhexyl)phthalate	4.2

The ingredients were mixed at room temperature and the solution was heated to 1150° F. and stirred for a period of about 24 hours. The resulting homogeneous solution had the following properties:

Viscosity at 140° F.	1895 centipoise.
Density at 140° F.	1.819 grams/cc.
Pour point	30° F.

This solution had a lower viscosity, density and pour point than a solution containing about the same amount of Kel-F #10 Oil or Kel-F 800 Resin (compare with Examples 10 and 11).

The following examples in Table V show properties of additional homogeneous solutions prepared by mixing Kel-F 800 Resin having a DSV of 0.5 with Kel-F #10 Oil.

TABLE V

HOMOGENEOUS SOLUTIONS OF KEL-F #10 OIL AND KEL-F 800 RESIN (DSV 0.5)

Example	Weight Percent Kel-F 800 Resin	DSV	Viscosity in cp./° F.	Density at ° F.	Pour Point ±5° F.
29	5.6	0.5	1,910/160	1.8943 at 160	45
30	4.6	0.5	1,101/160	1.8944 at 160	45
31	3.4	0.5	566/160	1.8895 at 160	40
32	1.8	0.5	277/150	1.8982 at 150	30
33	2.85	0.5	1,827/120	1.9720 at 120	40

It is to be understood, without departing from the scope of this invention, that any of the other normally solid polymers having a DSV between about 0.4 and about 3 may be admixed with any of the chlorofluorinated alkane oils, particularly any of the perchlorofluorinated alkane oils, having a minimum density of about 1.7 grams per cc. at 140° F. to provide highly viscous materials suitable for use as damping fluids, flotation fluids and highly viscous lubricants. The preparation of these viscous materials follows the method set forth in the application for which many modifications and embodiments may become apparent to those skilled in the art.

The fluid products of this invention find application as highly viscous thermally stable materials having low cloud points, low pour points and high density. These materials are well suited for use in gyro mechanisms of various design and in other similar applications such as, for example, in bi-metallic dial type thermometers and as chemical seal pulsation dampeners.

The products of this invention are also useful as chemical, thermal and shear resistant lubricants which have wide application in industry today.

Having thus described my invention I claim:

1. A homogeneous liquid solution for use as a gyro fluid which comprises a major amount of a perchlorofluorinated alkane oil having a minimum density of about 1.7 grams/cc. at 140° F. and containing between 4 and 22 carbon atoms per molecule and between about 2 and about 30 weight percent of a soluble, normally solid copolymer of chlorotrifluoroethylene and vinylidene fluoride having a dilute solution viscosity between about 0.2 and about 3 and containing between about 15 and about 35 mol percent vinylidene fluoride.

2. The homogeneous solution of claim 1 wherein the perchlorofluorinated alkane oil is a mixture of poly-

chlorotrifluoroethylenes having a molecular weight of between about 300 and about 500.

3. The homogeneous solution of claim 1 wherein the perchlorofluorinated alkane oil is a mixture of polychlorotrifluoroethylenes having a molecular weight of between about 500 and about 780.

4. The homogeneous solution of claim 1 wherein the perchlorofluorinated alkane oil is a mixture of polychlorotrifluoroethylenes having a molecular weight between about 780 and about 1,000.

5. The homogeneous solution of claim 1 wherein the perchlorofluorinated alkane oil is 1,1,3,5,6-pentachlorononafluorohexane.

6. The homogeneous solution of claim 1 wherein the perchlorofluorinated alkane oil is 1,1,3,5,7,8-hexachlorododecafluorooctane.

7. A homogeneous liquid solution for use as a gyro fluid which comprises a major amount of a perchlorofluorinated alkane oil having a minimum density of about 1.7 grams/cc. at 140° F. and containing between 4 and 22 carbon atoms per molecule; between about 2 and about 30 weight percent (based on said alkane oil) of a soluble, normally solid copolymer of chlorotrifluoroethylene and vinylidene fluoride having a dilute solution viscosity between about 0.2 and about 3 and containing between about 15 and about 35 mol percent vinylidene fluoride; and between about 0.5 and about 50 weight percent (based on the total weight of fluid components) of a hydrocarbon ester having between about 10 and 30 carbon atoms per molecule.

8. The homogeneous solution of claim 7 wherein the hydrocarbon ester is di-(2-ethylhexyl)phthalate.

9. In the method of operating a gyro mechanism containing a gyro operating in a fluid medium the improvement which consists of using as said fluid medium a homogeneous liquid solution comprising (1) between about 2 and about 30 weight percent of a soluble, normally solid copolymer of chlorotrifluoroethylene and vinylidene fluoride having a dilute solution viscosity between about 0.2 and about 3 and containing between about 15 and about 35 mol percent vinylidene fluoride, and (2) a major amount of a chlorofluorinated alkane oil having a minimum density of about 1.7 grams/cc. at 140° F. and containing between 4 and 22 carbon atoms per molecule.

10. In the method of operating the gyro mechanism containing a gyro operating in a fluid medium the improvement which consists of using as said fluid medium a homogeneous liquid solution comprising (1) between about 2 and about 30 weight percent of a soluble, normally solid copolymer of chlorotrifluoroethylene and vinylidene fluoride having a dilute solution viscosity between about 0.2 and about 3 and containing between about 15 and about 35 mol percent vinylidene fluoride, and (2) a major amount of a chlorofluorinated alkane oil having a minimum density of about 1.7 grams/cc. at 140° F., containing between 4 and 22 carbon atoms per molecule, and having an average molecular weight between about 300 and about 1000.

References Cited in the file of this patent

UNITED STATES PATENTS

2,583,588	Calvin	Jan. 29, 1952
2,584,222	O'Connor	Feb. 5, 1952
2,738,343	Dittmann et al.	Mar. 13, 1956
2,742,510	Davis	Apr. 17, 1956
2,748,098	Passino	May 29, 1956
2,766,157	Peterson	Oct. 9, 1956
2,770,615	Kroncke	Nov. 13, 1956
2,770,659	Barnhart	Nov. 13, 1956
2,837,550	Prober	June 3, 1958

FOREIGN PATENTS

734,644	Great Britain	Aug. 3, 1955
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【参考】米国特許 3076765 号の和文抄録

特許情報プラットフォーム（独立行政法人 工業所有権情報・研修館が運用）より、添付資料4の米国特許（US3076765）の和文抄録を入手した。

参照 URL : <https://www.j-platpat.inpit.go.jp/p0200>

【要約】

米国特許和文抄録

文献番号 : 3,076,765

特許日 : 1963.02.05

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発明の名称 高粘度の浮揚および制動液

抄録文

本発明の目的は、ジャイロ機構などのための浮揚および制動液として使用するのに適した高粘度の、低透明点を有し、高密度であり、さらに熱に安定な低分子量の過塩素フッ素化オレフィン重合体を提供することである。本重合体の出発物質は、約 $140 - 250^{\circ}\text{F}$ で融解し、 $\text{Y}(\text{CFCFC1}) \times \text{Z}$ の構造を有するクロロトリフルオルエチレンの均質重合体である。好ましいクロロトリフルオルエチレン重合体は U. S. P. 2, 770, 659 により提供されたような Y および Z がハロゲン原子（塩素およびフッ素）であるクロロトリフルオルエチレンのテロマーである。他の適当な出発物質として、ハロゲンおよび 1-4 個の炭素原子を有する脂肪族過ハロアルキル炭素化合物を含有するクロロトリフルオルエチレンのテロマーを含む。本発明の可溶性ポリクロロフルオルエチレンの製造方法は、上述の出発物質を約 $100 - 305^{\circ}\text{F}$ の間の温度を保つ適当な溶媒、たとえば脂肪族または芳香族のアルコール、ケトン、エーテル、エステルまたはハロ炭素に溶解する。この溶液の温度を室温程度まで下げ、生成した沈殿物および濾液を分離し、濾液から溶媒を除去する。本方法により得たポリクロロフルオルエチレンワックス製品は約 $100 - 215^{\circ}\text{F}$ の曇り点 210°F において約 1.905-1.930 の密度、また 210°F で約 205-700 センチストークスの粘度を有し、浮揚および制御液としてそのまま使用することが適当である。上述の可溶性ワックス製品に約 $90 - 140^{\circ}\text{F}$ の融点を有するポリクロロトリフルオルエチレンワックスを約 5-80 重量% 混合して使用することができる。出発物質として Ke 1-F 200 ワックス ($200 - 235^{\circ}\text{F}$ の融点を有する塩化スルフリルとクロロトリフルオルエチレンのテロマー) を使用した抽出ワックスの製造例を表に示してある。

特許情報プラットフォーム URL : <https://www.j-platpat.inpit.go.jp/>

以 上

United States Patent Office

3,076,765

Patented Feb. 5, 1963

1

3,076,765 HIGH VISCOSITY FLOTATION AND DAMPING FLUID

Fred W. West, Paterson, Raymond J. Seffl, Bloomfield, and Kenneth J. Reilly, Jersey City, N.J., assignors, by mesne assignments, to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware

No Drawing. Original application Feb. 15, 1957, Ser. No. 640,305. Divided and this application Dec. 11, 1957, Ser. No. 706,533

4 Claims. (Cl. 252-78)

This invention relates to a high viscosity material and to a method for the preparation thereof. In one aspect, this invention relates to a flotation agent for reducing frictional losses in instruments and machines. Another aspect of this invention relates to a damping agent for reducing impact and vibration damage and offers viscous non-elastic restraint to moving parts within a gyro. Another aspect of this invention relates to a halogenated, highly viscous material having high density and high shear stability. Still another aspect of this invention relates to a perchlorofluorinated damping and flotation agent for gyro mechanisms.

Gyro mechanisms which are used for controlling the operation of rockets, other aircraft and ships have now achieved wide recognition. A present day need for improved operating characteristics of gyros, is a highly viscous, high density material which is stable at high temperatures, that is, at temperatures of about 200° F. Various fluids and waxes have been employed for this purpose but these have not been able to meet all of the requirements demanded for a material of this type. Typical specifications for a gyro fluid are presented in Table I:

TABLE I

Temperature class	Viscosity, cp.	Density, g./cc.	Cloud point, ° F.
120° F.-----	3,000	1.958	<115
140° F.-----	>2,800	1.940	<135
160° F.-----	600	1.922	<155
160° F.-----	1,000	1.928	<155
160° F.-----	2,000	>1.930	<155

Other instruments such as the bi-metallic dial type thermometers and chemical seal pulsation dampeners have also indicated a need for a highly viscous material which meets most of the specifications mentioned above.

It is, therefore, an object of the present invention to provide a material having a high viscosity, a low clear point and a high density at elevated temperatures and to provide a method for the preparation thereof.

Another object of this invention is to provide a non-corrosive, thermally stable perchlorofluorinated olefin polymer suitable for use as a damping and flotation fluid.

Another object of this invention is to provide a perchlorofluorinated olefin polymer having a maximum clear point not in excess of 155° F.

Another object of this invention is to provide a low molecular weight perchlorofluorinated olefin polymer

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having a density of at least 1.949 grams per cc. at 140° F.

Another object is to provide a low molecular weight perchlorofluorinated olefin polymer having a viscosity of about 2800 cp. or higher at 140° F.

Another object is to provide a low molecular weight perchlorofluorinated olefin polymer suitable for use as a damping and flotation agent in a gyroscope.

Still another object of this invention is to provide a commercially feasible method for the preparation of a perchlorofluorinated olefin polymer damping and flotation agent having the above properties.

According to this invention a low molecular weight chlorotrifluoroethylene polymer having a melting point between about 140° F. and about 250° F. (ball and ring) is dissolved in a solvent, the temperature of the solution is lowered, the insolubles are removed from the solution leaving a filtrate and the soluble polymer product is recovered from the filtrate. The soluble polymer product which is recovered from the filtrate has a cloud point between about 100° F. and about 215° F. and a viscosity in excess of 200 centistokes at 210° F. This soluble wax product may be used directly as, for example, a specification gyro fluid, or it may be blended with a low molecular weight perhalogenated olefin polymer melting between about 90° F. and about 140° F. to obtain a product having the desired viscosity, density, cloud point and other requirements mentioned above.

The low molecular weight polymeric starting material of the present invention is the homopolymer of chlorotrifluoroethylene which melts at a temperature between about 140° F. and about 250° F. and which has the following formula



wherein x is an integer between 10 and 100 and Z and Y are selected from the group consisting of the halogens (fluorine, chlorine, bromine and iodine) and a perhalogenated alkyl radical.

The preferred chlorotrifluoroethylene polymer is the telomer of chlorotrifluoroethylene wherein Y and Z are normally gaseous halogen atoms (chlorine and fluorine) such as, for example, the telogen prepared from the reaction of chlorotrifluoroethylene with sulfur chloride, which telomer has a melting point between about 200° F. and about 235° F. (ball and ring). The preparation of this telomer is given in U.S. Patent No. 2,770,659.

Other suitable starting materials include the telomers of chlorotrifluoroethylene with halogens and aliphatic perhaloalkyl carbon compounds containing between 1 and 4 carbon atoms for example, fluorine, chlorine, bromine, iodine, bromochlorodifluoromethane, bromotrifluoromethane, chlorotrifluoromethane, bromotrifluoromethane, trichlorotrifluoroethane, pentachlorotrifluoropropane, etc. These telomers are prepared by cotelomerizing chlorotrifluoroethylene and the corresponding telogen in the presence of a peroxy compound. More specific details of the preparations are found in copending applications of William S. Barnhart, Serial No. 347,186 (filed April 6, 1953, now Patent No. 2,875,253) and Serial No. 452,708 (filed August 27, 1954, and now abandoned).

In the process of this invention the chlorotrifluoroethylene polymer is dissolved in a suitable solvent such as an aliphatic alcohol, ketone, ether, ester or halocarbon

or an aromatic alcohol, ketone, ether, ester or hydrocarbon. Examples of suitable solvents used in this invention include Cellosolve, dioxane, methyl phenyl ether, ethyl ether, ethyl phenyl ether, acetone, methyl ethyl ketone, acetophenone, isopropyl alcohol, diacetone alcohol, mineral spirits, methyl alcohol, benzyl alcohol, ethyl alcohol, ethyl acetate, methyl propionate, ethyl benzoate, carbon tetrachloride, trichloroethylene, chloroform, the Freons, toluene, xylene, etc., and mixtures of these solvents. The polychlorotrifluoroethylene is melted before it is admixed with the solvent.

Solvent to polymer ratios employed in this process can be varied between about 0.5:1 and about 20:1, preferably between about 1:1 and about 15:1. The chlorotrifluoroethylene polymer is generally dissolved at an elevated temperature such as for example, in a solvent which is maintained at a temperature of between about 100° F. and about 305° F. or at about the reflux temperature of the solvent. However, it is also within the scope of this invention to dissolve the polymer or fraction thereof in a solvent at room temperature (75° F.). The preferred method comprises dissolving the polymer in the solvent at a temperature of about 10° below the reflux temperature of the solvent but not at a temperature in excess of 305° F. While the polymer is being admixed with the solvent, it is generally preferred to agitate the mixture for a period of between about 10 minutes to about 10 hours. In most cases the mixture is agitated for a period not exceeding 2 hours. After the polymer is mixed with the solvent for the desired period of time, some insoluble material may still be present. These insolubles may be removed immediately if so desired.

The temperature of the solution of polymeric material prepared above at an elevated temperature is then lowered, preferably by allowing it to cool to about room temperature. However, in cases where the solution has been prepared at room temperature, the solution temperature is lowered for example, by a cold bath or by refrigeration usually to a temperature not below -10° C. and preferably not below 10° C. The lowering of the solution temperature results in the precipitation of insoluble materials. The insoluble material is removed as a residue by filtration, decantation or by any other convenient process or any combination of the above processes and the desirable polymer fraction or product which remains in the filtrate is recovered by evaporating, flashing off, fractionating, or distilling off the solvent or by the addition of water, if a water-soluble solvent is employed. The water takes up the solvent and can be decanted leaving a soluble polymer product, more specifically, a soluble wax product as the crude product of this invention. The crude soluble wax production is then dried.

When the desired wax product is recovered by the addition of water to the filtrate, the volume of water added to the filtrate can vary between about 0.05 and about 2 volumes or more, preferably between about 0.25 and about 1 volume of water per volume of filtrate. The soluble wax product so obtained is then dried to produce a wax product having a cloud point between about 100° F. and about 215° F. and a viscosity in excess of 200 centistokes at 210° F. If desired, the insoluble material which is removed after the solution temperature has been lowered can be reprocessed by redissolving it in a solvent; cooling the resulting solution; removing the insoluble materials and adding the resulting filtrate containing crude soluble wax product to the first filtrate before removing the solvent.

In one embodiment of the invention, the process is carried out by dissolving a liquid telomer of chlorotrifluoroethylene, melting between about 200° F. and about 235° F. in an aliphatic water-soluble solvent at the reflux tem-

perature of the solvent, or at a temperature 5° or 10° below the reflux temperature of the solvent employed. The solution is agitated at this temperature for a period of not more than 2 hours and then allowed to cool to room temperature. The resulting insoluble material, which is precipitated, is removed from the filtrate and water is added with agitation to the filtrate in a volume of between about 0.25 and about 1 volume of water for each volume of filtrate. After thoroughly mixing, the solid or crude product is allowed to settle, the liquors are removed and the remaining solvent is pressed from the soluble wax product so formed. The soluble wax product is then dried at a temperature between about 150° F. to about 250° F. for a period of from about 1 to about 16 hours under a pressure not in excess of about 300 mm. Hg, preferably not in excess of 175 mm. Hg.

In a preferred embodiment of the present invention the liquid telomer of chlorotrifluoroethylene obtained by melting the telomer is dissolved in a suitable solvent such as, for example, a toluene-isopropyl alcohol mixture, at an elevated temperature such as, for example at about 170° F. The solution is agitated for a period of not more than 2 hours and allowed to cool to room temperature. The resulting insoluble material, which precipitates, is removed from the filtrate and the soluble wax product is completely removed from the filtrate by distilling off the solvent.

The soluble wax product of this process, which has a cloud point between about 100° F. and about 215° F., a density between about 1.905 and about 1.930 at 210° F. and a viscosity between about 205 and about 700 centistokes at 210° F., is suitable for direct use as a flotation or damping agent or it can be blended with a lower molecular weight perhalogenated wax, such as polychlorotrifluoroethylene wax having a melting point between 90° F. and about 140° F. in amounts which vary from 100 weight percent to about 20 weight percent of the soluble wax product obtained above, preferably between about 40 weight percent to about 65 weight percent of soluble wax product obtained above. When the soluble wax product has a cloud point of 135° F. or above, it is usually desirable, in applications for gyro fluids, to blend the extracted wax products with a lower melting perhalogenated wax, melting between about 90° F. and about 140° F. for example, a polychlorotrifluoroethylene wax such as Kel-F 40 wax. The preparation of these low molecular weight, low melting polychlorotrifluoroethylene waxes is given in U.S. Patent No. 2,770,659.

The following examples are offered as a better understanding of the present invention and are not to be construed as unnecessarily limiting thereto.

The following example in Table II illustrates the preparation of the final extracted wax product of this invention. In the following example Kel-F 200 wax (the telomer of chlorotrifluoroethylene with sulfur chloride having a melting point from 200° F. to 235° F.) was dissolved in a water-soluble solvent at 175° F. Upon cooling the solution to room temperature the insoluble material was removed as a residue and the wax which remained in the filtrate was labeled Soluble Wax #1. The residue was dissolved in the same solvent at 175° F., the resulting solution was then allowed to cool to room temperature and the insoluble material was removed as the residue. The wax which remained in the filtrate was labeled Soluble Wax #2. The first and second filtrates are usually combined before removal of the solvent to obtain the soluble wax product, however, in the following example the two soluble wax products, which were separated from the filtrate by the addition of water, by decantation of the supernate and drying the product, were treated separately for comparison purposes.

TABLE II
Solvent Extraction of Kel-F 200 Wax

Ex. No.	Amount of Kel-F 200 Wax, g.	Solvent	Volume ratio solvent: wax	Components of Kel-F 200 Wax	Isolated yield, percent	Dynamic cloud point, ° F.	Viscosity, cs./° F.
1.....	1,000	Isopropyl alcohol.....	10:1	1st soluble wax..... 2nd soluble wax..... Residue.....	35.8 8.3 46.2	152 184	323.2/210 486.5/210

The cloud point was determined by slowly cooling a 15 gram sample of the final extracted wax product in a 25 x 150 mm. glass tube. All cloud points determined on waxes subsequently described were also carried out in this way.

preparation of the soluble wax product when reprocessing the residue is omitted and compares the properties of the product with the residue. In all the examples in Table III the soluble wax product was removed from the filtrate by distilling off the solvent.

TABLE III

Ex. No.	Amount of Kel-F 200 Wax, grams	Solvent	Volume ratio, solvent: wax	Components of Kel-F 200 Wax	Yield, percent	Cloud point, ° F.	Viscosity, cs./° F.	Density, g./cc. at 210° F.	Density, g./cc. at 140° F.
2.....	467	Isopropanol.....	2:1	Soluble wax product..... Residue.....	13.0 85.0	118 219	209.3/210	1.9128	
3.....	454	do.....	5:1	Soluble wax product..... Residue.....	27.4 71.2	134 226	252.9/210	1.9173	
4.....	469	Acetone.....	2:1	Soluble wax product..... Residue.....	48.8 45.2	156 244	401.9/210		
5.....	456	do.....	5:1	Soluble wax product..... Residue.....	65.1 26.1	169 270	415.0/210		
6.....	250	Isopropanol.....	10:1	Soluble wax product..... Residue.....	39.5 54.9	189 230	277/210	1.912	1.9705
7.....	250	do.....	15:1	Soluble wax product..... Residue.....	45.7 48.4	150 230	299/210		

¹ Calculated to be 12,000 cp. at 140° F. or 6,500 cs. at 140° F.

For comparison purposes, Kel-F 200 wax was tested and had a cloud point of 216° F.; a viscosity of 132.6 centistokes at 266° F. and a viscosity of about 950 centistokes at 210° F. Kel-F 40 wax (polychlorotrifluoroethylene wax having a melting point between about 90° F. and about 140° F.) was also tested and found to have a cloud point of 96° F., a viscosity of 37.97 centistokes at 210° F. and a density of 1.8792 at 210° F. Al-

40 The examples in Table IV below show additional experiments on the preparation of the soluble wax product using different solvents from those used in Table III. In the following examples (#8 through #23) the soluble wax product was separated from the filtrate by distillation. In Example #24 the soluble wax product was recovered by addition of water, decantation of the supernate and subsequent drying of the soluble wax product. 45

TABLE IV

Ex. No.	Amount of Kel-F 200 Wax in grams	Solvent	Volume ratio, solvent: wax	Yield of soluble wax, percent	Cloud point, ° F.	Viscosity			Density, g./cc.		
						210° F.	160° F.	140° F.	210° F.	160° F.	140° F.
8.....	200	Diacetone alcohol.....	5:1	25.9							
9.....	200	Cellosolve.....	5:1	31.4	130-35						
10.....	200	Methyl ethyl ketone.....	5:1	31.8	185-90						
11.....	200	Dioxane.....	5:1	60.4	165-70						
12.....	200	Mineral spirits.....	5:1	61.5	180-65						
13.....	200	Toluene.....	5:1	80.3	185-90	709.7 cs.					
14.....	200	Trichloroethylene.....	5:1	91.9	215-20				1.914		
15.....	200	Toluene.....	1:1	68.9	180-85	581 cs.			1.908		
16.....	200	do.....	1:1	79.0	185-90	538 cs.			1.932		
17.....	200	do.....	2:1	90.3	182-85	633 cs.			1.915		
18.....	200	do.....	4:1	92.5	185-90	549 cs.	5,500 cp.		1.9185	1.957	
19.....	200	do.....	5:1	47.3	145-50	343 cs.			1.9185		
20.....	200	20% toluene in i-PrOH.....	5:1	65.7	155-60	399 cs.			1.9187		
21.....	200	33 1/3% toluene in i-PrOH.....	5:2	79.3	160-65	445 cs.			1.9241		
22.....	200	40% toluene in i-PrOH.....	5:1	81.8	170-75	531 cs. or (1,014.8 cp.)					
23.....	200	50% toluene in i-PrOH.....	5:1	47.6	145-50	331.7 cs.	2,518.4 cs. or (4,918.3 cp.)			1.9529	
24.....	200	Isopropanol.....	10:1	35.9	137	278.....					

¹ The soluble wax product was recovered by the addition of water, decantation and drying of the wax product.

though according to gyro specifications the cloud point of Kel-F 40 wax is good, the viscosity and density is so poor that it would be unsuitable as a damping and flotation fluid for gyro mechanisms. As shown above, Kel-F 200 wax is deficient as a gyro fluid both in cloud point and in viscosity requirements.

The following examples in Table III illustrate the

70 Examples #25 through #44 in Table V below give the amount of material employed in the preparation of wax blends having the desired properties of the present invention. The extracted wax product was obtained from Kel-F 200 wax as described in the previous examples which employed a single extraction of the Kel-F 200 wax in solution. 75

TABLE V

Ex. No.	Soluble wax product obtained from example	Soluble wax product, grams	Kel-F 40 wax, grams	Cloud point, ° F.	Viscosity, cs.		Density, g./cc.			Viscosity, cp.			Viscosity cp./° F.
					140° F.	210° F.	140° F.	160° F.	210° F.	140° F.	160° F.	210° F.	
25	4	46.8	53.2	115-20	1,619	109.3	1.9520						
26	5	46.4	53.6	120-25	1,647	112	1.9560				3,160		
27	2	61.1	38.9	100-05	1,707	114.3	1.9545				3,220		
28	3	56.0	44.0	110-15	1,507	105	1.9501			1.8989	3,340		
29	7	52.1	47.9	115-20	1,638		1.9521			1.8956	2,940		
30	24	50.8	49.2	115-20	1,630		1.9523				3,190		
31	22	42.2	34.8	115-20	1,603.2		1.9522				3,180		
32	6	53.8	46.2	110-15	1,615	1104	1.9514	1.934	1.8931		3,065	1,100	189
33	6	57.2	42.8	115-20	1,700	1112	1.9544		1.894		3,150		
34	6	66.6	33.4	120-25	1,400	1135	1.954		1.895				12,500/115
35	6	80	20	125-30	1,370	1175	1.957		1.899				10,500/120
36	6	90	10	>135	1,500	1220	1.962		1.904				11,500/120
37	13	37.5	62.5	130-35	1,554		1.966		1.908		1,900		1,400/130
38	19	80	20	130-35			1.9500				3,035		
39	19	70	30	125-30			1.9620	1.946	1.9068		1,850	1,300	1,400
40	19	60	40	129-25			1.9570	1.9415	1.9025		1,650	1,230	1,314
41	23	80	20	130-35	3,726.5		1.9530	1.9375	1.8982		1,450	1,165	1,248
42	22	80	20	150-55							7,250		
43	22	70	30	140-45			1.952	1.941	1.9125		1,400	1,000	1,545
44	22	60	40	135-40			1.963	1.947	1.9075		1,850	1,300	1,410
							1.957	1.941	1.9015		1,620	1,250	1,310

¹ Calculated values.

It is to be understood without departing from the scope of this invention that any of the other polychlorotrifluoroethylene waxes melting between about 140° F. and about 250° F. (ball and ring), particularly polychlorotrifluoroethylene wax melting between about 140° F. and about 160° F. (Kel-F 10—200 Wax) can be extracted in accordance with the procedure set forth in any of the above examples to produce a wax product having the above described valuable properties; and that the wax products so produced can be employed per se or they can be blended with any of the perhalogenated waxes which melt between about 90° F. and about 140° F.

The products of this invention are particularly suited for use as damping and flotation fluids in gyro mechanisms since they meet all of the rigid requirements for gyro fluids. However, in addition to this application, the products of this invention may also be employed as damping fluids or flotation fluids in other applications such as, for example, chemical seal pulsation dampers, bi-metallic dial type thermometers, and other applications which require a highly viscous material which remains clear at low temperatures.

The extracted wax products or their blends may also be used as protective waxes for surfaces subject to corrosion, as packing material around pipe joints, etc. Many other applications of these products will be apparent to those skilled in the art from the accompanying description and properties of these materials.

This invention relates to the extraction and isolation of a soluble wax product from a mixture of a polychlorotrifluoroethylene wax (having a melting point between about 140° F. and about 250° F.) and an organic solvent for use in a particular application such as, for example, as a gyro fluid. The invention also relates to the mixing of the soluble wax product with a lower melting polychlorotrifluoroethylene oil (having a melting point between about 90° F. and about 140° F.) for use in a particular application such as, for example, as a gyro fluid.

This application is a division of copending United States patent application Serial No. 640,305, filed February 15, 1957.

Having thus described our invention we claim:

1. A damping and flotation fluid for gyro mechanisms and the like having a high viscosity, low clear point and

a high density which comprises a homogeneous mixture of (a) between about 5 and about 80 weight percent of a polychlorotrifluoroethylene wax having a melting point between about 90° F. and about 140° F., and (b) between about 95 and about 20 weight percent of a soluble polychlorotrifluoroethylene wax having a cloud point between about 135° F. and about 215° F. and a viscosity between about 205 and about 700 centistokes at 210° F., said soluble polychlorotrifluoroethylene wax being prepared by (1) dissolving a liquid chlorotrifluoroethylene polymer melting between about 140° F. and about 250° F. in an organic solvent selected from the group consisting of alcohols, ketones, ethers, esters, aliphatic halocarbons and aromatic hydrocarbons maintained at a temperature not in excess of 315° F., (2) lowering the temperature of the resulting solution to about room temperature to form a residue and a filtrate, (3) separating the residue from the filtrate and (4) removing the solvent from the filtrate to recover a soluble polychlorotrifluoroethylene wax product.

2. The damping and flotation fluid of claim 1 in which the preparation of said soluble polychlorotrifluoroethylene includes isopropanol as said organic solvent.

3. The damping and flotation fluid of claim 1 in which the preparation of said soluble polychlorotrifluoroethylene includes acetone as said organic solvent.

4. The damping and flotation fluid of claim 1 in which the preparation of said soluble polychlorotrifluoroethylene includes toluene as said organic solvent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,700,661	Miller	Jan. 25, 1955
2,770,659	Barnhart	Nov. 13, 1956
2,786,827	Barnhart	Mar. 26, 1957
2,806,866	Barnhart	Sept. 17, 1957
2,837,580	Barnhart	June 3, 1958

OTHER REFERENCES

"Kel-F" Technical Bull. No. 5-1-52 (4 pages), Chemical Manuf. Div., The M. W. Kellogg Co., Jersey City, N.J., May 1, 1952.

Zimmerman et al.: "Handbook of Material Trade Names," Supplement I, October 1956; Industrial Research Service Inc., Dover, N.H., page 117.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,076,765

February 5, 1963

Fred W. West et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 5 and 6, TABLE IV, Ex. No. 21, under the heading "Volume ratio, solvent: wax" for "5:2" read -- 5:1 --.

Signed and sealed this 17th day of September 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents