

United States Patent

[15] 3,638,308

Fischbein et al.

[45] Feb. 1, 1972

[54] **RAZOR BLADES**

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[58] Field of Search.....117/132 CF, 132 B, 161 KP, 117/161 UE; 260/77.5 AP, 77.5 CR; 30/346.53

2,612,484	9/1952	Bankoff	260/29.6
2,833,752	5/1958	Honn et al.	260/87.7
2,901,467	8/1959	Croco	117/132 X
2,929,800	3/1960	Hill	117/161 UX
2,937,976	5/1960	Granahan et al.....	117/132 UX
3,071,856	1/1963	Fischbein.....	117/132 X
3,071,858	1/1963	Alter.....	30/351
3,125,599	3/1964	Warnell	252/78 X
3,203,829	8/1965	Seyer et al.	117/132
3,250,808	5/1966	Moore et al.....	252/54.6 X
3,344,064	9/1967	Brady et al.....	117/161 X

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[56] **References Cited**

UNITED STATES PATENTS

3,386,962	6/1968	Damusis.....	117/161 X
3,410,817	11/1968	McClellan et al.....	117/132 X
3,345,202	10/1967	Kiss et al.....	117/132 X
3,402,468	9/1968	Kiss et al.....	117/132 X
3,342,875	9/1967	Selman et al.....	252/77 X

[57] **ABSTRACT**

The present invention is concerned with improving the shaving properties of razor blades. Generally the improvements are brought about by applying a solid, water-resistant polymeric polyether coating to the blade edge.

19 Claims, No Drawings

RAZOR BLADES

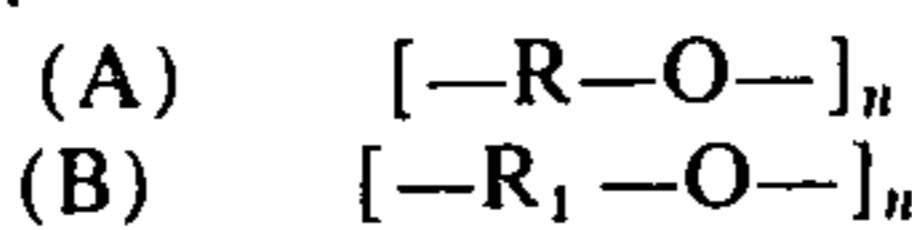
It is known that the shaving properties of razor blades can be appreciably enhanced by applying to the cutting edge polymer coatings such as polyfluorocarbons, e.g., polytetrafluoroethylene, as disclosed in U.S. Pat. No. 3,071,856 to Irwin W. Fischbein and organosiloxanes such as disclosed in U.S. Pat. No. 2,937,976 to Leon E. Granahan, Meyer J. Schnitzler and Edward M. Tuckerman. Although such polymer coatings have been in use for quite some time, it is still not completely understood how they function to bring about the improvement.

It has now been discovered that the shaving properties of razor blades may be appreciably enhanced by adhering a solid polyether polymer to the cutting edge. The improvement is characterized by a decrease in the force required to shave, which manifests itself in decreased pull and markedly increases comfort and ease. The reduction in pull may persist during several successive shaves with the same cutting edge, but it generally does not persist indefinitely. When the blades of the present invention are tested under carefully controlled conditions off the face, they require substantially less force to cut water-softened hair than do similar blades without the integument.

Generally the razor blades to which the present invention may be applied are usually about 0.0015 to about 0.015 inch thick and have wedge-shaped cutting edges, the included solid angle of which is greater than 14° and less than 35°. The faces or sides of such cutting edges extend back from the edge for a distance up to as much as 0.1 inch or even more. Each face need not be a single planar uninterrupted continuous surface or "facet," but many consist of two or more "facets" formed by successive grinding or honing operations and intersecting each other along zones generally parallel to the ultimate edge. The final facet, i.e., the facet immediately adjacent the ultimate edge, may have a width as little as 0.0003 inch or even less as compared to the diameter of a beard hair which averages about 0.004 to 0.005 inch, while the thickness of the ultimate edge itself is generally less than 6,000 Angstrom units and preferably less than 2,500 Angstrom units. The steel of which the blade edge is composed may be carbon steel, hardenable stainless steel, etc., and, if desired, it may be further coated with other metals or alloys such as chromium.

The polyether coating may extend over the entire wedge faces back from the ultimate edge or even farther, or it may cover only the portion of the final facet immediately adjacent to the ultimate edge. Generally with most coating techniques the coating will actually extend around the ultimate edge. Usually the thickness of the coating may be varied. Generally thin, continuous, adherent coatings having thickness for example in the order of a molecular monolayer up to 1 micron have been found effective.

Generally the polyethers which have been found useful in the present invention are the polyalkylene ethers and the polyperfluoroalkylene ethers. Generally polyalkylene ethers and polyperfluoroalkylene ethers may be represented by the following formulas:

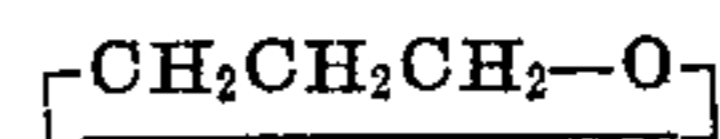


Wherein R is an alkylene group and more particularly an alkylene group comprising two to four carbon atoms; R₁ is a perfluoroalkylene group and more particularly a perfluoroalkylene group comprising two to three carbon atoms and n is the number of repeating units in the polymer. As examples of alkylene groups, mention may be made of ethylene, —CH₂CH₂—; 1,3-propylene or trimethylene, —CH₂CH₂CH₂— and tetramethylene, —CH₂CH₂CH₂—. As examples of perfluoroalkylene groups, mention may be made of tetrafluoroethylene, —CF₂CF₂— and 1,2-hexafluoropropylene, —CF₂—CF(CF₃)—. In the polyethers used in the present invention, the R and R₁ groups in a polymer chain may be the same or different, thus when desired copolymers may be employed.

Generally the polyalkylene ethers which have been found particularly useful in the present invention are the high molecular weight materials which can be caused to form on the cutting edge a water resistant, strongly adherent film which is not removed by water and which is not appreciably moved back from the cutting edge by the shaving action. Usually polyalkylene ethers comprising straight chain alkylene groups containing at least three carbon atoms such as those containing a preponderance of trimethylene or tetramethylene groups can be prepared as solid water resistant polymers. However, polyalkylene ethers such as polyethylene glycols are usually obtained as water soluble or water sensitive materials with little internal cohesive strength. In a preferred mode of carrying out the present invention, the polyalkylene ether glycols are linearly extended by reacting the terminal hydroxy groups with difunctional reagents in order to increase the length of the ether chain. In an especially useful embodiment of the present invention, the polyalkylene ether glycols are linearly extended by reagents which not only extend the length of the polyether chain but which also provide as a result of the reaction further reactive groups such as amino groups which can be used to cross-link the polyethers and strongly adhere them as water insoluble films, e.g., gels, on the cutting edge. As examples of such reagents, mention may be made of the diisocyanates. Such diisocyanates, as a result of the chain-extending reaction, provide secondary amino groups which can be reacted with further diisocyanates to cross-link the linearly extended ethers on the cutting edges.

In linearly extending the polyalkylene ethers it was found best to start with high molecular weight, e.g., greater than 1,540, polyethers so that the resulting linearly extended polymer would have characteristics closer to those of a polyether than a polyurethane. When using polyethylene glycols as the starting materials, particularly useful results were obtained using materials having molecular weights in excess of 3,000 and more particularly in excess of 5,000. Especially useful results were obtained using polyethylene glycols having molecular weight between about 6,000 to about 20,000, e.g., Carbowax 6,000 (M.W.—6,000) which is a polyethylene glycol sold by Union Carbide and Carbowax 20 M (M.W.—about 20,000) which is also sold by Union Carbide and is an epoxy-extended adjunct of the 6,000 M.W. polyethylene glycol.

Generally polyalkylene ether glycols for use in this present invention are readily available commercially or can be easily synthesized. For example, polyethylene glycols may be prepared by condensing ethylene oxide with ethylene glycol; polytrimethylene glycols can be obtained by polymerizing 1,3-propylene oxide,



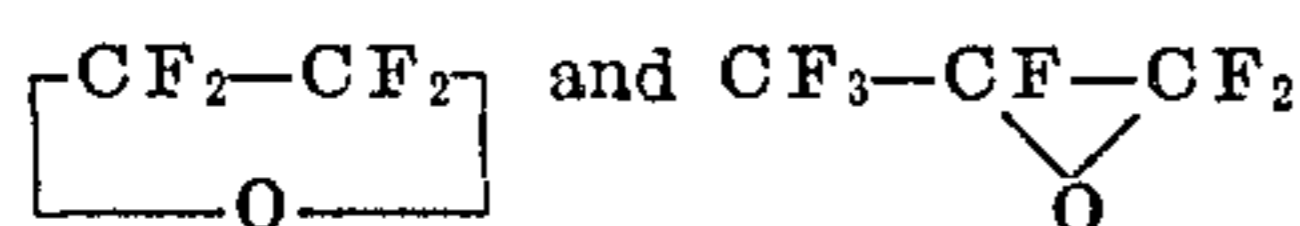
in the presence of a cationic catalyst such as boron trifluoride dihydrate (BF₃·2H₂O) and polytetramethylene glycols can be obtained by polymerizing tetrahydrofuran in the presence of a catalyst such as antimony pentachloride or phosphorous pentafluoride. The preferred polyalkylene ether glycols for use in this invention are those in which the alkylene group is in the form of a straight chain, e.g., ethylene, trimethylene, etc. Suitable chain-extending reagents such as the diisocyanates are also readily available. As examples of diisocyanates, mention may be made of tolylene -2,4-diisocyanate; naphthalene -1,5-diisocyanate; methylene -di-p-phenyl diisocyanate; 3,3'-dimethoxy -4,4'-biphenylene diisocyanate and hexamethylene 1,6-diisocyanate. Especially good results have been obtained using tolylene -2,4-diisocyanate and naphthalene -1,5-diisocyanate.

Generally the chain-extending reaction is best carried out in an inert solvent in which the resulting linearly extended polymer is soluble. As examples of useful solvents, mention may be made of dioxane and toluene. In carrying out the chain extending reaction and especially when using the diisocyanates, it has been found best to perform the reaction under

relatively mild conditions, e.g., at room temperature, so as to promote the production of the linearly extended polymer and to keep cross-linking of the polymer to a minimum. In using the diisocyanates at room temperature, it was found best to use greater than a 3 to 1 molar ratio of the diisocyanate to the glycol. In particularly useful embodiments, the diisocyanates are used in molar ratios ranging from about 5 to 20 moles of the diisocyanate to 1 mole of the glycol. Especially good results were obtained at about a 10 to 1 molar ratio. The chain-extending reaction is preferably only run to the point where all the hydroxy groups of the glycol have been reacted. Generally, by using the above ratios at room temperature, the chain-extending reaction will be completed in between about 15 to 30 days. The reaction can be greatly speeded up, however, by using a catalyst such as N,N-dimethylbenzylamine. Generally, using such a catalyst, all the hydroxy groups will be reacted in about 1 to 30 hours at room temperature.

Generally the linearly extended polyalkylene ethers can be applied to the cutting edges directly from the solutions in which they are prepared. In this manner the excess chain-extending reagent present can be used to gel or cross-link the linearly extended polymers and adhere it to the cutting edge without requiring any further additions. Good coatings were generally obtained by using about 1 to 10 percent by weight coating solutions. Once the coatings are applied to the cutting edge, the ethers may be gelled by heating the blades to an elevated temperature, e.g., 121° to 482° F. Particularly useful results were obtained by heating them to about 320° F. for about 30 minutes.

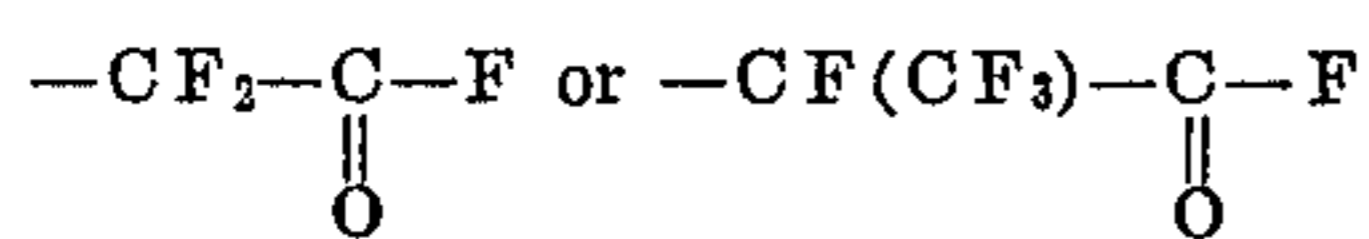
The polyperfluorocarbon ethers for use in the present invention may be prepared by processes such as disclosed in U.S. Pat. Nos. 3,125,599 and 3,250,808 wherein fluorocarbon epoxides such as



are polymerized in the presence of a suitable catalyst such as activated charcoal or an acid fluoride. Generally the polymers produced by such processes may be represented by the formula:



wherein R_f is a fluoro or trifluoromethyl radical and n is the number of repeating units in the polyether. Usually the ethers will be terminated on one end by a perfluoroalkyl group and on the other end by a perfluoroacid fluoride radical such as



When desired, the acid fluoride terminal group may be converted by well-known reactions to the corresponding carboxylic acid, salts of the carboxylic acid, an ester, an amide, etc., or it may be hydrogen capped by processes such as disclosed in U.S. Pat. No. 3,342,875. The polyperfluorocarbon ethers which are particularly useful in the present invention are those in which n is sufficiently high that the polyether is a solid. Especially useful results have been obtained with solid tetrafluoroethylene polyethers.

Generally the polyperfluorocarbon ethers are usually low melting (e.g., <212° F.), materials which are soluble in solvents such as FC 75 which is sold by 3 M Co. and is believed to be 2-n-perfluoropropyl-oxacycloperfluorohexane. This is in marked contrast to fluorocarbon polymers such as the polytetrafluoroethylenes which are often high melting (e.g., >572° F.), and not appreciably soluble in any known solvent. The solubility of the polyperfluorocarbon ethers in solvents plus their especially good ability to wet metals makes it quite easy to apply a continuous film of the polyether to the cutting edge. Generally, the concentration of the coating solutions may be varied to suit particular needs. Usually, good results may be obtained using about 1 percent to about 10 percent coating solutions.

Although the polyperfluorocarbon ethers of this invention can be formed on the cutting edge in continuous film without the need of subsequently heating them to their melting point in order to bring about coalescence, it has been found that best results are obtained by heating the films to temperatures which are usually substantially in excess of their melting points. Although heretofore it was thought the polyperfluorocarbon ethers were stable up to temperatures of 932° F., it was found that in the presence of the underlying metal edge that the polyethers unexpectedly are transformed by such heating into a gellike structure which is generally insoluble in the solvents in which the film was cast. Whether the transformation is due to intermolecular cross-linking within the film itself, to interaction, e.g., chemical bonding with the underlying metal edge, or to a combination of the two is not quite certain but for convenience the phenomena will be referred to herein as "cross-linking the polyether on the blade edge." Usually such transformation has generally taken place at temperatures in excess of 320° F. As a practical matter, the upper limit for carrying out the cross-linking step will usually be dictated by the temperatures which the underlying blade can be subjected to for short periods of time without unduly softening the metal, e.g., about 800° F. for stainless steel blades. Particularly good results were obtained by heating the polyperfluorocarbon ether films for about 30 minutes in an oven at temperatures between about 550° to 700° F. Preferably, the thermal cross-linking step is carried out in a protective atmosphere such as in a vacuum; in a reducing gas such as hydrogen or cracked ammonia; in an inert gas such as argon or nitrogen or in a slightly oxidizing atmosphere such as disclosed in copending U.S. application Ser. No. 644,052, filed June 7, 1967. An inert atmosphere of argon was found particularly useful.

In heating the polyperfluorocarbon ethers on to the blade edges, it has been found desirable, in certain instances, to carry out this step in the presence of a small amount of a free radical generator, e.g., 1 to 2 percent, based on the weight of the ether. It is believed that such free radical generator may, to some extent, help to linearly extend the ether and/or cross-link it to the blade edge. Generally, free radical generators are well known to the art. The preferred ones for use in this invention are those which will not readily evaporate at the temperatures involved in the heating step, e.g., high molecular weight organic hydroperoxides and peroxides such as cumene hydroperoxide, lauroyl hydroperoxide and dicumene peroxide.

Generally, in applying the polyether coatings of the present invention, the blades are sharpened in the usual manner and then washed at an elevated temperature, e.g., 150°-160° F., in a suitable solvent to remove residual grinding oils. As examples of useful solvents for washing the blades, mention may be made of tetrahydronaphthalene, decahydronaphthalene, benzyldimethyl amine, 2,2'-dichloroethyl ether and N,N-dimethylformamide which was found especially useful. The polyether coatings may be applied to the blade edges by any convenient method such as dipping, spraying, etc. In preferred embodiments, the solvents or vehicles which were used to apply the coatings are removed before subjecting the films to the heat treatments mentioned above. As can be appreciated, the solvents can be removed at room temperature or at elevated temperatures depending upon the particular solvent employed. Preferably, the heat treatment of the coatings is carried out in closed chambers where the atmosphere and temperature can be carefully controlled. When the heat treatment is carried out in a protective atmosphere at temperatures in excess of 300° F., it has been found best to first cool the blades to about 300° F. before exposing them again to the atmosphere. When desired, the coating steps may be repeated in order to increase the thickness of the coating on the blade edge.

The following nonlimiting examples illustrate the preparation of razor blades within the scope of the present invention:

EXAMPLE 1

A coating solution containing 5 percent polyethylene glycol (M.W. 6,000), 1.5 percent 2,4-toluene diisocyanate (about a 10 to 1 molar ratio of the diisocyanate to the glycol) and 0.08 percent benzyldimethyl amine in dioxane was made up and allowed to react at room temperature for 1 hour. A supply of carbon steel blades which had been washed in N,N-dimethyl formamide were dipped into the solution and heated in a forced air oven for 30 minutes at 320° F. The resulting blades were tested against uncoated blades on a shave test panel and were rated markedly better for shaving comfort and ease by a substantial majority of the shavers.

EXAMPLE 2

A coating solution was made up similar to that of example 1 except that the molar ratio of diisocyanate to glycol was about 7 to 1. The solution was split up and portions were reacted for periods varying from 5 to 24 hours at room temperature. A series of carbon steel blades were coated with the various solutions and heated at 320° F. for 30 minutes. When the blades were shave tested against uncoated blades, they were rated markedly better by a substantial majority of the shavers.

EXAMPLE 3

A series of solutions was made up similar to example 2 except that the molar ratio of diisocyanate to glycol was about 17 to 1. The solutions were reacted over the periods ranging from one-half to 7 hours and coated on a series of carbon steel blades which were then cured in a manner similar to example 2. The blades were rated markedly better than the uncoated control blades by a substantial majority of the shave test panel.

EXAMPLE 4

A coating solution was made up similar to that of example 1 except that 1,5-naphthalene diisocyanate was used in place of the 2,4-toluene diisocyanate at a molar ratio of 10 to 1 to the glycol. The solution was reacted for 2 hours at room temperature and coated on a group of carbon steel blades which were then cured for 30 minutes at 320° F. in a forced air oven. The resulting blades were rated markedly better than the untreated control blades by a substantial majority of the shave test panel members.

EXAMPLE 5

Blades were prepared in a manner similar to that of example 4 except that the amount of 1,5-naphthalene diisocyanate was reduced to a 5 to 1 molar ratio. The resulting blades were rated substantially better than the untreated controls by a substantial majority of the shave test panel members.

EXAMPLE 6

A group of carbon steel blades were coated with a solid polytrimethylene glycol which was prepared by ring-opening 1,3-propylene oxide in the presence of boron trifluoride. The coatings were cured on the blades for 20 minutes at 320° F. The resulting blades, when shave tested, were preferred over the untreated control blades by an appreciable majority of the shavers.

EXAMPLE 7

A dioxane coating solution containing 5 percent of Carbowax 20-M and 1.15 percent of 2,4-toluene diisocyanate was made up and allowed to stand for 23 days at room temperature. A gelled solution which could be liquified by agitation resulted. Carbon steel blades were dip coated in the liquified solution and cured for 10 minutes at 320° F. When the blades were shave tested, they were preferred over the uncoated control blades by an appreciable majority of the test panel participants.

EXAMPLE 8

A group of stainless steel blades were dip-coated into a 2-n-perfluoropropyl-oxacycloperfluorohexene coating solution containing 1 percent of a solid polytetrafluoroethylene oxide polymer. The coated blades were heated in an argon atmosphere for 30 minutes at 700° F. As a result of the heating, the polytetrafluoroethylene ether coating underwent a transformation so that it was no longer soluble in the 2-n-perfluoropropyl-oxacycloperfluorohexane. When the blades were tested by cutting wet, matted hair, it was found that they accomplished the cutting with less than 50 percent of the force which was needed with cleaned, uncoated control blades. In a shave test against uncoated control blades, they were rated superior by a substantial majority of the shavers.

EXAMPLE 9

Two set of blades were prepared in a manner similar to that of example 9 except that one set was heated in hydrogen instead of argon and the other set was heated in nitrogen instead of argon. The blades were rated comparable to the argon cured blades in both the shave test and the matted hair cutting test.

EXAMPLE 10

A group of stainless steel blades which had been cleaned in trichloroethylene were dipped for 10 seconds in a solution containing 10 cc. of 1,1,2-trichloro-1,2,2-trifluoroethane, 5 gm. of Fomblin Y (heavy), a polyhexafluoropropylene oxide polymer obtained from Peninsular Chemresearch Co. and 0.08 gm. of cumene hydroperoxide. The dipped blades were placed on a spindle in spaced apart relationship and heated in argon at 550° F. for 10 minutes. The blades were redipped in the solution and heated once again in argon at 550° F. for 30 minutes. When the blades were shave tested, they were rated markedly better than the uncoated control blades by a substantial majority of the shave test participants. They also required substantially less force to cut wet, matted hair than the uncoated control blades.

Having thus described the invention, what is claimed is:

1. A razor blade having on its cutting edge an adherent, solid, water-resistant coating comprising a polyether polymer, said polyether polymer being selected from the group consisting of polyalkylene ethers and polyperfluorocarbon ethers, the alkylene radicals of said polyalkylene ethers comprising two to four carbon atoms and the perfluorocarbon radicals of said polyperfluorocarbon ethers comprising two to three carbon atoms.
2. A blade as defined in claim 1 wherein said polyether is a polyperfluorocarbon ether.
3. A blade as defined in claim 2 wherein said polyperfluorocarbon ether is a polytetrafluoroethylene ether.
4. A blade as defined in claim 2 wherein said polyperfluorocarbon ether is a polyhexafluoropropylene ether.
5. A blade as defined in claim 2 wherein said polyperfluorocarbon ether is thermally cross-linked on the cutting edge.
6. A blade as defined in claim 5 wherein said polyperfluorocarbon ether is a polytetrafluoroethylene ether.
7. A blade as defined in claim 5 wherein said polyperfluorocarbon ether is a polyhexafluoropropylene ether.
8. A blade as defined in claim 6 wherein said cross-linking is carried out at a temperature between about 320° F. to about 800° F.
9. A blade as defined in claim 7 wherein said cross-linking is carried out at a temperature between about 320° F. to about 800° F.
10. A blade as defined in claim 5 wherein said polyperfluorocarbon ether was heated on the blade edge in the presence of a free-radical generator.
11. A blade as defined in claim 1 wherein said polyether is a polyalkylene ether.

12. A blade as defined in claim 11 wherein said alkylene groups are straight-chained alkylene groups.

13. A blade as defined in claim 11 wherein said polyalkylene ether is a linearly extended polyalkylene glycol.

14. A blade as defined in claim 13 wherein said polyalkylene glycol is linearly extended with a diisocyanate. 5

15. A blade as defined in claim 13 wherein said linearly extended polyalkylene glycol is cross-linked on the blade edge.

16. A blade as defined in claim 15 wherein said polyalkylene glycol is linearly extended and cross-linked with a 10

diisocyanate.

17. A blade as defined in claim 16 wherein said polyalkylene glycol is a polyethylene glycol having a molecular weight in excess of 1,540.

18. A blade as defined in claim 17 wherein said polyethylene glycol has a molecular weight in excess of 5,000.

19. A blade as defined in claim 18 wherein said polyethylene glycol has a molecular weight between about 6,000 to about 20,000.

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