ADHERENT COATING OF CURED SOLID HYDROCARBON POLYMER CONTAINING A CHAIN OF CARBON ATOMS INCLUDING A PLURALITY OF $\text{-CH}_2\text{-CH}_2\text{-}$ GROUPS.
RAZOR BLADE HAVING A COATING OF A CURED SOLID HYDROCARBON POLYMER ON ITS CUTTING EDGE

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11 Claims. (Cl. 30—251)

This invention relates to safety razors and pertains more specifically to a blade, either single edged or double edged, having a cutting edge on which is an adherent coating comprising a solid hydrocarbon polymer containing a chain of carbon atoms including a plurality of —CH₃—CH₂— groups, which coating improves the shaving effectiveness of the blade edge, and to a method for making a blade having such a coated edge.

Oily or greasy safety razors are known in which a hydrous dispersion of a hydrocarbon polymer may be employed in the present invention to produce improved blades are from 0.003 to 0.015 inch (about 75 to 375 microns) 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 some such cutting edges extend back from the ultimate 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 may consist of two or more "facets" formed by successive grading 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 7.5 microns or even less as compared to the diameter of a hair which averages about 100 to 125 microns, while the thickness of the ultimate edge itself is generally less than 0.6 micron and preferably less than 0.25 micron. The steel of which the blade edge is composed may be either carbon steel or stainless steel. In either case it is hardened by a suitable process, as by heat-treating or working. There is a limit to the extent to which the blade subsequently may be heated since excessive reheating will lead to loss of hardness. As a general rule the heat-hardened metal blade edges cannot be subjected to a temperature above about 400° F. for more than five minutes without some tempering or softening, although work-hardened blades edges can withstand considerably higher temperatures. In some cases, however, particularly with stainless steel, some softening or tempering of the blades can be tolerated since its disadvantages are more than offset by the improvement in shaving effectiveness produced by the present invention. Moreover, the coating may also be applied to blades having cutting edges of (or coated with) metals or metal alloys other than steel or stainless steel.

As is well known, such conventional steel razor blades despite their sharpness cannot be employed for shaving a dry beard without excessive shaving cream or soap. The pain and irritation produced by shaving a dry beard are due to the excessive force required to draw the cutting edge of the blade through the unsoftened beard hairs. When force is transmitted to the nerves of the skin adjacent the hair follicles from which the beard hairs extend, and, as is well known, the irritation produced by excessive pulling of these hairs may continue for a considerable period of time after the pulling has ceased.

It has now been discovered that by providing on the cutting edge of a safety razor a thin layer or coating comprising a solid hydrocarbon polymer containing a chain of carbon atoms including a plurality of —CH₃—CH₂— groups, which is adherent to the blade, there results a remarkable increase in shaving effectiveness of the blade. This increase in effectiveness is characterized by a decrease in pull; that is, a decrease in the force required to cut the beard hairs, which becomes apparent in the noticeably increased ease of shaving, making it possible, if desired, to abbreviate the customary beard-softening step which precedes shaving. The blades of the present invention when tested under severely con- trolled conditions of the face require much less force to cut water-softened hair than do similar blades without the coating on the cutting edge. This reduction in pull may persist during several successive shaves with the same blade cutting edge, although it does not persist indefin- itely.

The drawing is a schematic representation of the razor blade of the present invention.

The solid hydrocarbon polymer coating may extend over the entire wedge faces back from the ultimate edge or even further, or it may cover only a portion of the final facet.

Razor blades of the present invention which possess excellent shaving properties exhibit a pattern of spectral interference fringes (when examined at a magnification of several hundred diameters using vertical illumination with white light and with the observed surface oriented parallel to the optical axis of the microscope), the total number of fringes observed in the area extending back 0.002 inch from the ultimate edge of these blades averaging 4 to 10, although blades exhibiting a single fringe or more are also excellent. These fringes indicate a change in thickness of the coating, the order of colors signifying the direction of change. In some cases the coating increases gradually in thickness to a maximum thickness of about 0.4 to 1.0 micron at a distance of about 0.0005 inch from the ultimate edges, then decreases gradually to a thickness of less than 0.002 inch at a distance of 0.001 inch from the ultimate edges. In other cases the thickness continues to increase gradually for a much greater distance, reaching as much as 0.002 micron, for example, at a distance of 0.002 inch from the ultimate edge. In arriving at these values, a refractive index of 1.5 and a half-wave length for white light of 3000 angstroms were used. The thickness of the coating need not be uniform throughout its extent.

The hydrocarbon polymers which may be used in practicing the present invention are solid materials containing a chain of carbon atoms, either linear (straight chain) or branched chain, the linear polymers generally being preferred, including a plurality of —CH₃—CH₂— groups. Homopolymers of ethylene, as well as copolymers of ethylene with a minor proportion of other monomers such as propylene or butene, have been found effective, and polymers of butadiene (1,4-addition, also mixed 1,4- and 1,2-addition) when hydrogenated to the extent of about 85% to 90% or more of the theoretical amount possible, have been found effective. Polyethylene may also be used as the polymer. Good results have been achieved with both high-density and low-density polyethylene, but high-density polyethylene is preferred. Mixtures of two or more of any of the foregoing polymers may be employed; indeed, some such mixtures give enhanced results. The polymers may vary widely in molecular weight in the form in which they are used for applying to the cutting edge, and good results have been obtained with polymers that were commercially available to the applicant which had number-average molecular weights of the order of 3000 and more.

The hydrocarbon polymers useful in the present invention can be applied to the blade from a solution or dispersion in a suitable volatile liquid such as toluene, xylene, perchloroethylene, etc. The solution or dispersion of polymer may be applied to the cleaned faces of the razor blade edge by dipping or immersing the blade edge...
In the solution or dispersion which is heated, by spraying it onto the edge as by nebulization, by flowing it onto the edge from a capillary, or by stopping it on. Alternate methods of applying the polymer include fluidized-bed or melt-coating techniques, and flame spraying.

After application of the polymer to the blade, it is cured by any suitable means as by heating under oxidizing conditions at an elevated temperature to bond it firmly to the substrate and to render it effective for improving the shaving characteristics of the blade. Depending upon the identity of the particular polymer used, the time of heating in air may vary from half an hour to a few hours or even less to as little as half an hour at a temperature of 300°F. to 320°F. Other temperatures may also be employed, but lower temperatures generally require longer times. If the supply of oxygen is restricted, as by heating the coated blades in a partial vacuum or in mixtures of air with inert gases, or if the effect of the oxygen is inhibited by the presence of antioxidants in the polymer coating, longer times or higher temperatures, or both, will be required. It is also possible to shorten the times or decrease the temperatures by introducing into the polymer coating an oxidation catalyst such as cobalt naphthenate.

It is important, however, that the curing be not continued to the point at which the coating is degraded or chemically or physically altered to the extent that the desired improvement in shaving effectiveness is lost. In the case of many polyethylene which are free from or contain only very small amounts of additives which inhibit cure, heating the coated blades for an hour in air at 320°F. results in overcure and loss of the improved shaving effectiveness. In order to provide closer control over extent of cure, it may be desirable to preheat blades before the composition is applied to the cutting edge and to cool the blades in, for example, circulating cool air immediately after the termination of the curing step.

While the behavior of the polymer coating during the heating or curing step may not be fully understood, it is believed that the polymer undergoes an oxidation reaction resulting in cross-linking and oxidative degradation. As the oxidation proceeds, the strength of the adhesive bond to the cutting edge increases and the physical and chemical structure of the coating gradually changes, reaching optimal properties for shaving purposes at some stage during the oxidation. Further oxidation results in a gradual decrease of the desirable coating properties and finally results in a coating which produces no detectable improvement in shaving characteristics.

Achieved have been those with polyester coatings which, after curing on the blade edge, contain 10% or more by weight of crystalline material as measured by X-ray diffraction. This crystallinity is of the polyethylene crystalline habit. The extent of crystallinity for any given coating decreases as the extent of cure increases.

The resultant thin adherent coating, which is given mechanical support throughout its extent by the underlying blade, reduces the pull during the shaving operation and increases the ease of shaving.

It should be noted that while the increased shaving effectiveness of the present invention is obtained by proper curing of a hydrocarbon polymer alone on the blade cutting edge, other materials may be present without having any significant adverse effect upon the shaving effectiveness. Dyes, slip agents, some antioxidants and the like can be incorporated in the polymer, for example, and various oils and greases which may or may not contain anticorrosion agents and which are normally applied to the blade may in some cases flow over the outer exposed face of the cured polymer coating. The latter materials are simply wiped on after the blade or during the first stroke in shaving, leaving the properly cured polymer coating to accomplish the desired result. Other polymers, which are by themselves ineffective for the purpose of the present invention, may be mixed with the hydrocarbon polymers described above in minor proportions without destroying the increase in shaving effectiveness; indeed, in some cases, enhancement of the effect upon shaving characteristics is produced by the addition. Among polymers which may be used as blending partners, the hydrocarbon polymers are polyisobutylenes, poly(butene-1), poly(4-methylpentene-1), butyl rubber, polypropylene, Hevea rubber, polybutadiene, poly(vinylisobutylenes), etc. Polyisobutylenes, indeed, may be present in major proportion, as much as 90% (by weight) or more, such as a modifier, and its addition in certain proportions produces a noticeable enhancement of shaving effectiveness.

The following specific examples are illustrative of the nature of the present invention. Blades treated in accordance with each of the examples were found by actual shave tests to have remarkably improved shaving characteristics as compared with like blades untreated.

Example 1

A sample of branched-chain low-density polyethylene having a number-average molecular weight of about 7000 and a high melt index (390) (DYLTLT, Union Carbide Plastics Co.) was dissolved in hot xylene to form a 0.5% solution by weight. Uncoated Gillette steel razor blades (0.004 inch thick, bladed) were cleaned thoroughly by washing with hot benzene and drying; their cutting edges were then dipped into the polymer solution at 284°F. and after removal the coating remaining on the edges was dried at room temperature. The coated blades were then mounted on pairs of steel spindles, each blade being spaced 9/4 inch from the blade below it in the stack by a pair of 9/8 inch diameter washers so as to ensure uniform heating. A holder carrying seven such pairs of spindles with their stacks of blades arranged so that the edges of successive stacks were about 1/4 inch apart and having a total loaded weight of approximately 650 g. was placed in a hot air oven (Blue M Model OV-490, Blue M Electric Co.) set at 320°F. and allowed to remain for ten minutes. The blades exhibited two interference fringes in the zone extending back 0.001 inch from the ultimate edge. Other blades were treated in the same manner as the first set, except that the heating time was fifteen minutes instead of ten, and except that they exhibited three interference fringes instead of two.

Example 2

A sample of a linear high-density (0.95) copolymer of a major proportion of ethylene with a minor proportion of butene-1 having a number-average molecular weight of about 7300 and a melt index of 6.5 (Marlex 5005, Phillips Chemical Co.) was dissolved in hot xylene to form a solution containing 0.5% by weight. Uncoated Gillette steel razor blades (0.004 inch thick, bladed), cleaned thoroughly by washing in trichloroethylene and drying, were then coated as described in Example 1 and dried. Specimens of the blades were then heated by mounting them on a stainless steel conveyor belt provided with pairs of projecting nips for holding blades in position on its upper horizontal face with their edges parallel to the direction of advance and mounted so that it advanced the blades continuously into, through and out of an elongated heater. The blade width was less than half the width of the blades and approximately 0.05 inch thick, the nips being arranged so that successive blades were spaced apart by somewhat less than 3/4 inch. The heater, a three-foot long generally rectangular mass of aluminum weighing many times as much as an equal length of band and blades, had a longitudinal internal central passage only slightly greater in cross section than the band with the blades carried by it. Electrical heating elements were provided along the top and bottom of the heater, the temperature being controlled by thermocouples seated in wells in the heater walls adjacent the passage. The speed
of the band was adjusted so that each blade required three minutes to pass through the heater, which was maintained at 320°F. The blades exhibited three interference fringes in the zone 0.001 inch back from the ultimate edge. Other specimens of the same blades were treated in the same manner, except that they were in the heater for one-half minute and one minute, respectively.

Additional specimen, coated as described in this Example 2, were heated as described in Example 1 above (except that the oven used was Blue M Model OV-500, Blue M Electric Co.) for ten minutes, fifteen minutes, and thirty minutes, respectively. All of these blades exhibited shawling characteristics even better than those of Example 1, the best results being obtained at cure times of one to ten minutes.

Still other specimens, cleaned and coated as described in this Example 2, were heated as described in the paragraph immediately preceding, except that the oven was set for 248°F and some of the specimens were heated for five hours while the remainder were heated for twenty-four hours.

All of the blades after curing exhibited 2 to 5 fringes in the zone extending 0.001 inch back from the ultimate edge of the blade.

**Example 3**

A sample of the copolymer described in Example 2 was dissolved in hot xylene to form a solution containing 0.75% by weight. Uncoated Gillette steel razor blades as described in Example 2 were cleaned and coated with this solution in the manner described in that example and dried. Specimens of these blades were heated at 320°F, in the same manners and for the same time periods as those heated at 320°F in Example 2. The blades exhibited 10 interference fringes in the zone extending 0.002 inch back from the ultimate edge, indicating a gradual increase in thickness to that point.

**Example 4**

A sample of a linear high-density (0.95) copolymer of a major proportion of ethylene with a minor proportion of butene-1 having a number-average molecular weight of about 10,000 and a melt index of 0.3 (Marlex 5003) was dissolved in hot xylene to form a 0.5% solution by weight. Uncoated Gillette steel razor blades as described in Example 2 were cleaned and coated with this solution in the manner described in that example. The coated blades were heated at 320°F in the same manners and for the same times as those heated at 320°F in Example 2. The blades exhibited 2 to 5 interference fringes in the zone extending back 0.001 inch from the ultimate edge.

**Example 5**

A sample of linear high-density (0.96) polyethylene having a number-average molecular weight of about 8100 and a melt index of 5.0 (Marlex 6050) was dissolved and applied to blades and heated as described in Example 4.

**Example 6**

A sample of linear high-density (0.96) polyethylene having a number-average molecular weight of about 13,000 and a melt index of 0.2 (Marlex 6002) was dissolved and applied to blades and heated as described in Example 4.

**Example 7**

A sample of the copolymer described in Example 2 was dissolved in hot xylene to form a solution containing 0.5% by weight. To this solution molybdenum disulfide powder (MoS₂, The Alpha-Molykote Corporation) was added to form a suspension containing 0.02% by weight of the disulfide. This suspension which was kept dispersed by stirring, was applied to the blades in the manner described in Example 2. Some blades were heated for ten minutes and the remainder for fifteen minutes at 320°F. In the Blue M oven identified in Example 2. The blades after heating exhibited ten interference fringes in the zone extending back 0.001 inch from the ultimate edge, the first five of these fringes nearest the ultimate edge indicating an increase in coating thickness, and the other five indicating a decrease in thickness.

**Example 8**

A sample of the copolymer described in Example 2 was dissolved in hot xylene to form a solution containing 0.5% by weight. N-tallow trimethylenediamine (Duomeen T, Armour & Co.) was dissolved in this solution to form a solution containing 0.005% by weight. This solution was applied to the blades and heated in the manner described in Example 2. The blades after heating exhibited eight interference fringes in the zone extending back 0.001 inch from the ultimate edge, the first four of these fringes nearest the ultimate edge indicating an increase in coating thickness and the other four indicating a decrease in thickness.

**Example 9**

Uncoated Gillette stainless steel razor blades made from Uddeholm AEB stainless steel which contains 13% chromium, 1% carbon, 1% manganese and .15% silicon were cleaned and coated as described in Example 2. The blades were then heated for 10 minutes at 320°F in the Blue M oven identified in Example 2. The blades after heating exhibited four interference fringes in the zone extending back 0.001 inch from the ultimate edge, the first two of these fringes nearest the ultimate edge indicating an increase in coating thickness and the other two indicating a decrease in thickness.

**Example 10**

A sample of an intermediate density (0.93) polyethylene with a melt index of 3.0 (Alathon 34, E. I. du Pont de Nemours & Co., Inc.) was dissolved in hot xylene to form a solution containing 0.5% by weight. Uncoated Gillette steel razor blades (0.004 inch thick, blue) were cleaned and coated with this solution as described in Example 2. The blades were then heated for three minutes at 320°F using the band apparatus of Example 2. The blades after heating exhibited eight interference fringes in the zone extending 0.001 inch from the ultimate edge, the first four of these fringes nearest the ultimate edge indicating an increase in coating thickness and the other four indicating a decrease in thickness.

**Example 11**

A sample of an intermediate density (0.93) polyethylene with a melt index of 3.0 and containing a “slip” agent (Alathon 34A, E. I. du Pont de Nemours & Co., Inc.) was applied to uncoated Gillette steel razor blades in the same concentration and manner as described in Example 10. The blades after heating exhibited eight interference fringes in the zone extending 0.001 inch from the ultimate edge, the first four of these fringes nearest the ultimate edge indicating an increase in coating thickness and the other four indicating a decrease in thickness.

**Example 12**

A linear high-density (0.94) polyethylene of very high molecular weight (weight-average molecular weight of over 2 million; Hi-Fax 1901, Hercules Powder Company) was dissolved in boiling decalin to form a solution of 0.05% by weight. Uncoated Gillette steel razor blades were treated with this solution in the manner described in Example 10. The blades after heating exhibited no interference fringes in the region extending 0.002 inch from the ultimate edge, indicating that the thickness did not reach as much as 0.2 micron anywhere in this area.

**Example 13**

A sample of a partially hydrogenated polybutadiene (1,4-polymer) with about 11% residual unsaturation (Hy-
dropol I, Phillips Petroleum Company) having a weight-average molecular weight of about 100,000-150,000 was dissolved in hot xylene to form a 0.5% solution by weight. The blades were coated and heated as described in Example 1 (except that the solution temperature was 212° F. and the oven used was Blue M Model OV-500, Blue M Electric Co.) for 10 minutes. The blades after curing exhibited one fringe in the zone extending 0.001 inch back from the ultimate edge of the blade.

Example 14
A sample of a block copolymer consisting of 66% ethylene and 34% propylene was dissolved in hot xylene to form a 0.25% solution by weight. The blades were coated and heated as described in Example 13. The blades after curing exhibited one fringe in the zone extending 0.001 inch back from the ultimate edge of the blade.

Example 15
There were dissolved in 200 cc. of hot xylene 0.65 g. of the polyethylene described in Example 5 and 0.35 g. of polylubutylene of viscosity-average molecular weight of about 120,000 (Vistamex LM-120, Enjay Chemical Co.). Different lots of the blades were coated and heated as described in Example 13 for 5, 10, 15 and 20 minutes respectively. The blades after heating exhibited six interference fringes in the zone extending back 0.001 inch from the ultimate edge, the first three of these fringes nearest the ultimate edge indicating an increase in coating thickness and the other three fringes indicating a decrease in thickness. Other polyisobutylene products having viscosity-average molecular weights from 80,000 to 330,000 also were found to be satisfactory in admixture with polyethylene.

Example 16
There were dissolved in 200 cc. of hot xylene 0.65 g. of the copolymer described in Example 2 and 0.35 g. of the first polyisobutylene described in Example 15. Blades were coated and heated as described in Example 15. The finished blades exhibited the same fringe pattern as the blades of Example 15.

Example 17
There were dissolved in 200 cc. of hot xylene 0.4 g. of the polyethylene described in Example 5 and 0.6 g. of the first polyisobutylene described in Example 15. The blades were coated and heated as described in Example 13 but for 15 minutes. The blades after heating exhibited four fringes in the zone extending back 0.001 inch from the ultimate edge, the first two of these fringes nearest the ultimate edge indicating an increase in thickness and the other two fringes indicating a decrease in thickness.

Example 18
There were dissolved in 200 cc. of hot xylene 0.9 g. of the polyethylene described in Example 5 and 0.1 g. of a 95% cis-1,4 polybutadiene of Mooney viscosity greater than 40 ml. at 212° F. (“Clis-4” rubber, Phillips Petroleum Co.). The blades were coated and heated as described in Example 13 for 10 minutes. The blades after heating showed six fringes in the zone extending back 0.001 inch from the ultimate edge, the first three of these fringes nearest the ultimate edge indicating an increase in thickness and the other three fringes indicating a decrease in thickness.

Example 19
To the solution described in Example 15 was added .01 g. of a polymer antioxidant 4,4’-thiodis (6-tert-butyl meta-cresol) (Santonox, Monsanto Chemical Co.), and this solution was applied to blades and the blades heated as described in Example 13 but for 30 minutes. The blades after heating exhibited four fringes in the zone extending back 0.001 inch from the ultimate edge, the first two of these fringes nearest the ultimate edge indicating an increase in thickness and the other two fringes indicating a decrease in thickness.

Example 20
There were dissolved in 200 cc. of hot xylene 1.4 g. of the polyethylene described in Example 5, 0.6 g. of the partially hydrogenated polybutadiene described in Example 13, and 0.01 g. of the antioxidant described in Example 19. The blades were coated and heated as described in Example 13 but for 15 minutes. The blades after heating exhibited one fringe in the zone extending back 0.001 inch from the ultimate edge of the blade.

Example 21
There were dissolved in 200 cc. of hot xylene 0.95 g. of the polyethylene described in Example 5 and 0.05 g. of poly( vinylisobutylen ether) (Oppanol CKV125, Badische Anilin- & Soda-Fabrik A.G.). The blades were coated and heated as described in Example 13 but for 15 minutes. The blades after heating exhibited six interference fringes in the zone extending back 0.001 inch from the ultimate edge, the first three of these fringes nearest the ultimate edge indicating an increase in thickness and the other three fringes indicating a decrease in thickness of the film.

This application is a continuation-in-part of my copending application Serial No. 154,894, filed November 24, 1961.

Although specific embodiments of the invention have been described herein, it is not intended to limit the invention solely thereto, but to include all of the variations and modifications which suggest themselves to persons skilled in the art.

What is claimed is:
1. A safety razor blade having on its cutting edge an adherent coating comprising a cured solid hydrocarbon polymer containing a chain of carbon atoms including a plurality of —CH=—CH2— groups.
2. A safety razor blade as claimed in claim 1 in which said polymer has a molecular weight at least of the order of 5,000.
3. A steel safety razor blade having on its cutting edge an adherent coating comprising a cured solid polymer of ethylene.
4. A razor blade as claimed in claim 3 in which said polymer has a molecular weight at least of the order of 5,000.
5. A steel safety razor blade as claimed in claim 3 in which said polymer is a homopolymer of ethylene.
6. A steel safety razor blade as claimed in claim 5 in which said coating comprises polyisobutylene in addition to said homopolymer.
7. A steel safety razor blade having on its cutting edge an adherent coating comprising a cured solid copolymer of ethylene and butene.
8. A steel safety razor blade as claimed in claim 7 in which said coating comprises polyisobutylene in addition to said copolymer.
9. A razor blade as claimed in claim 1 in which said blade is steel and said polymer is a partially hydrogenated polymer of butadiene.
10. A steel safety razor blade as claimed in claim 9 in which said coating comprises a cured solid homopolymer of ethylene in addition to said hydrogenated polymer.
11. A razor blade as claimed in claim 1 in which said blade is steel and said polymer is a copolymer of ethylene and propylene.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,071,858

January 8, 1963

Harvey Alter

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.

Column 1, line 27, for "buy" read -- but --; line 45, for "blades" read -- blade --; column 2, line 24, for "while" read -- white --; lines 34 and 36, for "edges" read -- edge --; lines 57 and 58, for "polyethylene" read -- polyethylenes --.

Signed and sealed this 2nd day of July 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents