LUBRICANT COATED FORMABLE METAL ARTICLE

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6 Claims. (Cl. 29—195)

This invention relates to an improved formable metal article. In particular, this invention relates to a formable article comprising a metal substrate having an improved metal-working lubricant coating thereon. In addition this invention relates to an improved process for forming a metal article.

In cold-working operations for forming metals, such as drawing, stamping, coinining, rolling, forging, swaging, extruding and modifications thereof, where metal is formed by exertion of pressure upon the metal by a metalworking tool, a considerable amount of the total work expended to achieve the desired resultant shape of the metal is used to overcome the friction between the metal and the metal-working tool. Metal articles coated with several types of metal-working lubricants have been used with varying degrees of success in reducing the friction in metal forming operations. However, a need exists for a more readily formable metal article, that is, a metal article treated in such a manner so as to considerably reduce the amount of work required to overcome friction in a metal-working operation.

An object of this invention is to provide a readily formable metal article having a coating thereon which will provide a formable article comprising a metal substrate having an improved metal-working lubricant coating thereon. A further object is to provide an improved process for forming a metal article.

These and other objects are attained by a coated metal article having substantial bulk, the dimensions of which are alterable by a cold forming operation, said article having a coating thereon which comprises 50—95% by weight of petroleum wax and 5—30% by weight of a normally solid polymer containing at least about 60% by weight of an olefin having 2—4 carbon atoms.

The term “forming,” as used herein, refers to any cold metal-working process, including the so-called primary working processes whereby articles such as ingots, billets, or powder compacts are converted to mill products such as bars, beams, plates, tubes, rods, strips, sheets and the like. Primary working processes include cold rolling, cold forging, cold swaging, cold drawing, cold extrusion and modifications thereof. “Forming” also encompasses the so-called secondary working processes whereby mill products are formed into useful articles of manufacture. Secondary working processes include stamping, drawing, coining and other such forming operations. The process used should be operated at a temperature below the melting point temperature of the petroleum wax to avoid liquefication thereof. Generally, operation at a temperature of below about 125° F. is satisfactory.

All metals which are formable by cold metal-working processes are usable in this invention. Some of these metals are titanium, zirconium, vanadium, tantalum, chromium, molybdenum, iron, nickel, platinum, copper, silver, gold, zinc, cadmium, aluminum, tin, bismuth, and other soft metals including brass, bronze and the like and the ferrous metal alloys such as the various carbon and stainless steels. Particularly adaptable for use in the practice of this invention are formable sheets which comprise a ferrous metal substrate having a ferritic chromium containing alloy coating. Such alloy coated products may be produced by various methods familiar to the art, for example, by the adhesive bonding or cladding of a chromium alloy coating onto the ferrous metal substrate, or by chromium diffusion-coating processes.

Any normally solid polymer containing at least about 60% by weight of an olefin having 2—4 carbon atoms may be used in this invention. As used herein, the term “normally solid” is synonymous with “nonliquid at room temperature (i.e. about 25° C.).” Thus, a polymer which has the physical characteristics commonly associated with a grease may be used in this invention. However, it is generally preferable to use a polymer which has a greater degree of solidity than a grease. In other words, the preferred polymers are those which have the physical characteristics of soft waxes, hard waxes, soft resins, hard resins, and so forth.

Molecular weight and degree of crystallinity are two important variables which affect the solidity of the polymer. In the case of polypropylene, for example, the polymers which have a fairly high degree of crystallinity, such as the isotactic polymers, and which have a molecular weight of at least about 1,000 possess the preferred degree of solidity. The amorphous polymers such as atactic polypropylene do not have a specific minimum molecular weight which marks a distinct separation between normally solid and normally non-solid phases. Generally, the liquid atactic propylene polymers are those with molecular weights below about 300 to 500. While the degree of solidity of the polymer increases with increasing molecular weight, even atactic polypropylene with a molecular weight of several thousand exhibits cold flow. However, atactic polypropylene with a molecular weight of at least about 1,000 usually is sufficiently solid to be useful in this invention. In other words, the lower limit of the molecular weight depends on the particular polymer employed. There is no upper limit as to the molecular weight of the polymers used in this invention.

The polymers of this invention include the homopolymers of olefins containing 2—4 carbon atoms, that is, polyethylene, propylene, polypropylene, polisobutylene, etc., and copolymers such as olefins with other copolymerizable monomers, for example, vinyls such as vinyl acetate and vinyl chloride, vinyl acrylates and methacrylates, carboxylic acids such as methacrylic acid, and other copolymerizable monomers including styrene and acrylonitrile. The term “olefin” refers not only to those hydrocarbons having one olefinic double bond, but also to the dienes such as butadiene. A mixture of two or more of these olefin polymers may be used if desired so long as the metal working lubricant contains 5—50% by weight of at least one of the described polymers. It is essential that the polymer used be normally solid and it must contain at least about 60% by weight of an olefin having 2—4 carbon atoms. Particularly preferred species of this invention are those employing a propylene polymer or an ethylene/vinyl acetate copolymer.

Some of the polymers of this invention are not completely compatible with petroleum wax. Compatibility is a function of both the type of polymer used and the amount of copolymer blended with the wax. In the case of ethylene/vinyl acetate copolymers, for example, blends of 50—95% by weight of petroleum wax and 5—50% of a copolymer containing either 15—25% or 33—40% of vinyl acetate, have a haze point which varies from about 5° C. to 30° C. or more above the melting point of the wax depending on the particular composition of the blend. It is not essential that the wax-polymer blends used in the practice of this invention be completely compatible. Thus, ethylene/vinyl acetate copolymers containing 15—40% by weight of vinyl acetate (i.e., about 60—85% ethylene) are useful in this invention. However, it is generally preferable to use more compatible blends, in particular those in which the copolymer contains 25—33% by weight of...
vinyl acetate. Vinyl acetate content of the copolymer may be determined by infrared analysis or by saponifica-
tion-number determination.

The various methods of preparation of the polymers used in this invention are well known to those skilled in the art. The particular process employed is not critical, thus any convenient procedure can be used, for example as described in Sittig, Polyolefin Resin Processes, Gulf Publishing Company, Houston, 1961, and also in U.S.P. 2,153,553, U.S.P. 2,200,429, U.S.P. 2,274,749, U.S.P. 3,051,690; and elsewhere.

The term "petroleum wax" as used herein refers to both paraffin and microcrystalline wax. Paraffin wax is a mixture of solid hydrocarbons derived through the frac-
tional distillation of petroleum. After purification paraf-
fin wax contains hydrocarbons that fall within the for-
mulas C22H44-C30H60. It is a colorless, hard and trans-
lucent material having a melting point of about 125-
165° F. Microcrystalline wax is also obtained through
petroleum distillation. It differs from paraffin wax in
having branched hydrocarbons of higher molecular
weights. It is considerably more plastic than paraffin wax
and has a melting point of about 150-200° F.

Polyethylene wax-blends which are used in this
invention contain from about 50% to 95% by weight
of petroleum wax and from about 5% to 50% by weight of
polymer. These blends may be prepared in any con-
venient manner known in the art such as shown in U.S.P.
2,595,911 and British Patent 887,417.

In the practice of this invention, a metal article is
coated with the wax-polymer blend by any suitable pro-
cedure. For example, a metal article may be dipped into
a hot melt of such a blend, or a solvent solution of the
blend may be prepared which can be used to coat the
metal by dipping, spraying or brushing techniques. To
insure adequate adherence of the coating to the metal
article, it is usually preferable to precoat the metal article
to remove foreign matter such as grease, grit and the like.
The required thickness of the coating depends upon the
specific operating conditions, such as the particular metal
article used, the forming process employed, and so forth.
Therefore, the amount of the wax-polymer blend to be
applied to the metal article is determined by trial and prac-
tical experience, however, for most cases, the coating
should be at least 1 mil thick. After the coating has been
applied, the metal article may be formed as desired.

The primary purpose of the coatings of this invention
is to serve as a metal-working lubricant. In normal in-
dustrial practice, the coating is removed from the metal
after the article has been formed. One convenient manner
by which the wax-polymer coatings may be
removed is by first subjecting the coated articles to tem-
peratures slightly above the melting point of the petroleum
wax and permitting the coating to flow off of the article;
subsequently, any of the wax-polymer which remains on
the article may be burned off. The wax-polymer blends
of this invention are soluble in several common solvents
such as benzene, toluene, xylene, and trichloroethylene, and
therefore these coatings may easily be removed by a
solvent washing procedure. Before and after forming,
care should be taken to avoid baking the coating or other-
wise subjecting the coating to conditions which would
promote crosslinking of the polymer chains in the wax-
polymer blend to thereby insolubilize the coating.
Avoiding this heating, i.e., less than 1 mil thick,
and elevated temperatures, usually prevents such cross-
linking and thus insures that the coating will be readily
removable.

The advantages obtained by this invention are illustrated
by the following series of examples. Two standard tests
are used in these examples:

**Olsen Cup Test**

This test is conducted in accord with ASTM 20, Part
II, 398. A lubricated metal blank of about four square
inches is clamped between a die and ball of given radius.
The ball is hydraulically forced through the blank causing
it to stretch. To compare the lubricating effect of vari-
ous coatings, several runs are made with different con-
coatings using the same die, ball, and type of metal blank.
Since the die, ball, and metal blank are constant, the
depth of the cup to rupture is dependent on the effective-
ness of the lubricating coating.

** Ericksen Deep Draw Test**

In conducting this test, a circular lubricated metal blank
of a given diameter is hydraulically clamped between a
punch and die. The punch forces the metal through the
die and a cup is thereby formed. This cup is then redrawn
with a smaller diameter punch and die. Variables mea-
sured as a function of the lubricating effect of the coating
are: the force required to make both draws, which should
be a minimum; and, the depth to which the second draw
is made prior to rupture, which should be a maximum.
Further details of this test are given in the Metals Hand-
Society for Metals. In the following examples, the hy-
draulic clamping pressure in each instance was 2,420
pounds.

The following examples are intended only to illustrate
this invention and are not intended to impose any limita-
tions on the scope thereof.

**Example 1**

This example shows the performance of two standard
metal-working lubricants commonly used heretofore.

In all the tests shown in this example and in Examples
2-5 shown hereinafter, SAE 1008 aluminum-killed draw-
ing steel, 0.026 inch thick, was used. In each test, the
steel was treated, prior to coating, as follows: The steel
samples were first degreased in trichlorehylene vapor,
and then pickled in 6 N HCl for one minute. Pickled
samples were thoroughly washed in running water, and
then rinsed in acetone and forced air dried.

For this example, different samples were coated with
tallow and graphite grease. Samples with a 72 mm. diam-
eter were deep drawn in an Erickson machine. The sam-
ple coated with tallow required an average drawing force of
3660 lbs./in.² for the first draw while the sample coated
with graphite grease required an average drawing force of
3510 lbs./in.² for the first draw. Other samples at
least 90 mm. square were cupped to rupture in an Olsen
machine. The sample coated with tallow gave an aver-
age cup depth of 423 mils, and the sample coated with
graphite grease an average cup depth of 418 mils.

In view of the above data, tallow coated samples were
used as the standard of comparison in the Olsen Cup Test
in the following examples, while the graphite grease
coated samples were used as the standard of comparison
in the Ericksen Deep Draw Test.

**Example 2**

Two solvent solutions of ethylene/vinyl acetate-wax
blends were prepared as follows: 45 parts by weight of
a blend consisting of 30% by weight copolymer and 70%
vinyl acetate was dissolved in 55 parts of toluene; the second
solution was prepared by dissolving 40 parts of a blend
consisting of 70% copolymer and 30% wax in 60 parts
toluene. The copolymer used in both solutions was an
ethylene/vinyl acetate copolymer having a vinyl acetate
content of 28%, by weight, and a melt index of 15. The
two solutions were maintained at temperatures of
60° C. and 70° C. respectively. Panels of the SAE 1008
aluminum-killed drawing steel, described above, having
a surface area of 90 square mm. were treated as shown in
Example 1 and were coated with both solutions and
dried to remove all toluene. The blend containing
30% copolymer gave an average coating thickness of
2.2 mils. The blend containing 70% copolymer
 gave an average coating thickness of 1.4 mils. The sam-

ples were evaluated by the Olsen Cup Test method, giving the results tabulated in Table I. All figures in Table I represent an average of 3 tests.

**TABLE I**

<table>
<thead>
<tr>
<th>Coating composition:</th>
<th>Olsen cup depth, mils</th>
<th>423±3</th>
<th>455±2</th>
<th>439±6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tallow</td>
<td>30% copolymer-70% wax</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70% copolymer-30% wax</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table I shows the significant improvement over standard lubricants, which is obtained by steel coated with a blend of 30% ethylene/vinyl acetate copolymer and 70% paraffin wax.

**Example 3**

Circular samples of the treated steel described in Example 1, having diameters of 72 mm, were dipped in the coating solutions described in Example 2. These samples were subjected to the Erickson Deep Draw Test, the results of which are summarized in Table II. All figures shown in Table II represent an average of 5 tests. As shown in Table II, the steel coated with the blend of 30% ethylene/vinyl acetate copolymer-70% paraffin wax gave a decided improvement over the steel coated with a standard lubricant, requiring 265 lb./in.² less force for the first draw and 670 lb./in.² less force for the redraw, and giving a cup depth of over twice that obtained with the graphite grease, and without rupture.

The steel coated with the blend of 70% copolymer and 30% paraffin wax ruptured on the first draw. In other words, metal coated with such a blend is actually not as satisfactory as metal coated with standard lubricants known in the art, and hence, is outside of the scope of this invention.

**Example 4**

Example 3 is repeated using in place of the aluminum-killed drawing steel shown therein, degreased circular samples of a ferritic chromium-containing alloy diffusion coated steel 0.026 inch thick having a diameter of 72 mm. Similar results are obtained.

**Example 5**

Example 3 is repeated using in place of the ethylene/vinyl acetate copolymer shown therein, polyisobutylene having a molecular weight of about 10,000. Similar results are obtained.

**Example 6**

In all of the tests of this example SAE 1008 aluminum-killed drawing steel 0.020 inch thick was used. Panels of this steel were prepared by degreasing in trichloroethylene vapor. For Test 1, panels of the prepared steel were coated by dipping into the solution of 30% copolymer and 70% wax described in Example 2 giving an average coating thickness of 1.5 mils. For Test 2, panels were coated by dipping into the solution of 70% copolymer and 30% wax described in Example 2 giving an average coating thickness of 1.5 mils. For Test 3, panels were coated by dipping into a toluene solution containing 20% by weight of an ethylene/vinyl acetate having a vinyl acetate content of 28% by weight and a melt index of 15. This solution was maintained at 70° C. The average coating thickness was 1.5 mils. For Test 4, the panels were not coated. For Test 5, panels were coated by dipping into a hot melt of paraffin wax. These wax coatings were thick and nonuniform. In all of these tests, the panels were evaluated by the Olsen Cup Test method, the results of which are shown in Table III. All results shown in Table III represent an average of 3 tests.

**TABLE II**

<table>
<thead>
<tr>
<th>Coating Comp.</th>
<th>Force to Draw, lb./in.²</th>
<th>Rupture, Average Depth, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Draw with 35 mm. punch</td>
<td>Redraw with 35 mm. punch</td>
<td></td>
</tr>
<tr>
<td>Graphite grease</td>
<td>2.50±0.19</td>
<td>4.80±0.39</td>
</tr>
<tr>
<td>30% Copolymer-70% wax</td>
<td>3.34±0.47</td>
<td>9.80±0.82</td>
</tr>
<tr>
<td>70% Copolymer-30% wax</td>
<td>3.60±0.90</td>
<td>Did not rupture, all drew greater than 50 mm.</td>
</tr>
</tbody>
</table>

The comparative data of Table III illustrate that the copolymer-wax blends of this invention give an unexpected improvement over the use of copolymer alone, wax alone, and also over the use of copolymer-wax blends containing greater than 50% by weight of copolymer.

**Example 7**

Two solvent solutions of paraffin wax-polypropylene were prepared as follows: 45 parts by weight of a blend consisting of 10% by weight of an atactic polypropylene having a molecular weight of ca. 6,000 and 90% paraffin wax was dissolved in 55 parts by weight of toluene at 60°-70° C; the second solution was prepared by dissolving 45 parts of a blend consisting of 30% by weight of an atactic polypropylene having a molecular weight of ca. 6,000 and 70% by weight of paraffin wax in 55 parts of toluene at 60-70° C. Panels of the SAE 1008 aluminum-killed drawing steel, described in Example 1 having a surface area of 90 square mm. were treated as shown in Example 1 and were coated by dipping into the solutions and then dried to remove all toluene. The thickness of the coatings obtained thereby, varied from 1.1 to 1.5 mils as between different panels. These coated panels were evaluated by the Olsen Cup Test method, giving the results tabulated in Table IV. All figures in Table IV represent an average of 3 tests.

**TABLE IV**

<table>
<thead>
<tr>
<th>Coating composition:</th>
<th>Olsen cup depth, mils</th>
<th>423±3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tallow</td>
<td>90% wax-10% atactic polypropylene (M.W. 6,000)</td>
<td>448±6</td>
</tr>
<tr>
<td></td>
<td>70% wax-30% atactic polypropylene (M.W. 6,000)</td>
<td>463±6</td>
</tr>
</tbody>
</table>

**Example 8**

Two solvent solutions of paraffin wax-polypropylene were prepared as follows: 45 parts by weight of a blend
TABLE VI

<table>
<thead>
<tr>
<th>Test</th>
<th>Coating Composition</th>
<th>Force to Draw, lb./in.²</th>
<th>Rupture, Average Depth, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Draw with 33 mm. punch</td>
<td>Redrawn with 20 mm. punch</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Graphite Grease</td>
<td>3,810±119</td>
<td>4,520±171</td>
</tr>
<tr>
<td>2</td>
<td>70% Wax-30% Atactic Polypropylene (M.W. 6,000)</td>
<td>3,435±43</td>
<td>4,350±147</td>
</tr>
<tr>
<td>3</td>
<td>70% Wax-30% Atactic Polypropylene (M.W. 12,000)</td>
<td>3,145±60</td>
<td>4,400±176</td>
</tr>
<tr>
<td>4</td>
<td>70% Wax-30% Isotactic Polypropylene (M.W. 100,000)</td>
<td>3,235±25</td>
<td>4,100±130</td>
</tr>
</tbody>
</table>

consisting of 10% by weight of an atactic polypropylene having a molecular weight of ca. 12,000 and 90% paraffin wax was dissolved in 55 parts by weight of toluene at 60–70°C; the second solution was prepared by dissolving 45 parts of a blend consisting of 30% by weight of an atactic polypropylene having a molecular weight of ca. 12,000 and 70% by weight of paraffin wax, in 55 parts toluene at 60–70°C. Panels of the SAE 1008 aluminum-killed drawing steel, described in Example 1 having a surface area of 90 square mm, were treated as shown in Example 1 and were coated by dipping into the solutions and then dried to remove all toluene. The thickness of the coatings varied from 1.1 to 1.5 mils between panels. These coated panels were tested by the Olsen Cup Test method, giving the results shown in Table V. All figures in Table V represent an average of 3 tests.

**TABLE V**

<table>
<thead>
<tr>
<th>Coating composition:</th>
<th>Olsen cup depth, mils</th>
</tr>
</thead>
<tbody>
<tr>
<td>90% wax-10% atactic polypropylene (M.W. 12,000)</td>
<td>440±21</td>
</tr>
<tr>
<td>70% wax-30% atactic polypropylene (M.W. 12,000)</td>
<td>463±6</td>
</tr>
</tbody>
</table>

**Example 9**

Circular samples of the SAE 1008 aluminum-killed drawing steel described in Example 1, having diameters of 72 mm., were treated as shown in Example 1. For Test 1 of this example, samples of this treated steel were coated with graphite grease to provide a standard of comparison with the following tests. For Test 2, steel samples were coated by dipping in the solution of 70% paraffin wax and 30 atactic polypropylene (molecular weight of 6,000) described in Example 7. For tests, steel samples were coated by dipping in the solution of 70% paraffin wax and 30 atactic polypropylene (molecular weight of 12,000) described in Example 8. For Test 4, steel samples were coated by dipping into a solution of 15 parts by weight of a blend consisting of 70% paraffin wax and 30% of an isotactic polypropylene having a molecular weight of ca. 100,000, dissolved in 85 parts of toluene at 110°C. All of these coated samples were evaluated by the Ericksen Deep Draw Test, the results of which are shown in Table VI. The results shown in Table VI represent an average of 5 tests.

Other normally solid polymers containing at least 60% by weight of an olefin having 2–4 carbon atoms, including polyethylene, ethylene/ethyl acrylate copolymers, isobutylene/styrene copolymers, polybutadiene, butadiene/styrene copolymers, and the like, give similar results. I claim:

1. A coated metal article having substantial bulk, the dimensions of which are alterable by a cold forming operation, said article having on its surface a metal working lubricant coating comprising 50 to 95% by weight of petroleum wax and 5 to 50% by weight of a normally solid polymer containing at least 60% by weight of an olefin having 2 to 4 carbon atoms.

2. The article of claim 1 wherein the said polymer is an ethylene/vinyl acetate copolymer containing 60–85% by weight of ethylene.

3. The article of claim 1 wherein the said polymer is an ethylene/vinyl acetate copolymer containing 65–75% by weight of ethylene.

4. The article of claim 1 wherein the polymer is polypropylene.

5. A formable article having substantial bulk, the dimensions of which are alterable by a cold forming operation comprising a ferrous metal substrate having a ferric chromium-containing alloy coating, and having a metal working lubricant coating superposed thereon which comprises 50–95% by weight of petroleum wax and 5–50% by weight of a normally solid polymer containing at least 60% by weight of an olefin having 2–4 carbon atoms.

6. The article of claim 5 wherein the polymer is an ethylene/vinyl acetate copolymer containing 65–75% by weight of ethylene.

**References Cited by the Examiner**

**UNITED STATES PATENTS**

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Year</th>
<th>Invention</th>
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<tbody>
<tr>
<td>2,530,838</td>
<td>11/1950</td>
<td>Orozco --- 72—42 X</td>
</tr>
<tr>
<td>3,078,237</td>
<td>2/1963</td>
<td>Creech et al. --- 252—59 X</td>
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<tr>
<td>3,084,128</td>
<td>4/1963</td>
<td>Stillwagon --- 117—132</td>
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