

3,287,264

COATING COMPOSITIONS

Harry Hyman Topper, Manchester, England, assignor to Imperial Chemical Industries Limited, Millbank, London, England, a corporation of Great Britain
 No Drawing. Filed Mar. 18, 1964, Ser. No. 352,961
 Claims priority, application Great Britain, Nov. 28, 1958, 38,442/58; Nov. 12, 1962, 42,618/62
 27 Claims. (Cl. 252-28)

This is a continuation-in-part of copending U.S. application Serial No. 854,586, filed November 23, 1959, now abandoned, and Serial No. 316,123, filed October 14, 1963.

This invention relates to coating compositions for metals to facilitate the formation of the metals into shaped objects.

Metals in various forms, and particularly in sheet form are employed for a wide variety of industrial applications such as pressing and forming. Coating compositions are sometimes applied to the metals to preserve them from damage during storage as for example from mechanical abrasion or from corrosion. In the pressing or forming operations it is also common practice to coat the die, punch, or other forming device with a lubricant, and also to apply a lubricant to the metal. However, frequent lubrication is necessary and this slows down the speed with which the press or other forming device can be operated. Even when conventional lubricants are employed, splitting and scoring of the metal may occur during the forming operation, and to avoid this it is also common practice to anneal the metal between each step of the forming operation. Frequent annealing is undesirable because it adds greatly to the cost of manufacture.

It has now been found that the necessity for lubricating the die of the press or other forming device and for applying lubricants to the metal immediately before pressing can be avoided by employing certain coating compositions for the metal, which compositions behave as lubricants during the pressing or forming operation. The use of these coating compositions also enables the number of annealing operations to be reduced, and decreases defects such as scoring and splitting.

The coating compositions we employ are solutions in an organic solvent of a copolymer of an acrylic or methacrylic ester with minor amount of a carboxylic acid containing an ethylenically unsaturated linkage to which solution may be added in minor amount, a proportion of an organic solvent soluble alkylated heat hardenable condensation product of formaldehyde with urea or melamine, and/or a proportion of a mineral lubricant such as graphite and/or an oily or waxy lubricant of the kind commonly employed to reduce metal to metal friction and/or a chlorinated paraffin as described further herein.

According to the present invention we provide an improved process for pressing or forming metals which comprises the steps of applying to the metals a coating composition as defined above, removing the solvent therefrom and thereafter converting the coated metal into a shaped object by pressing or forming.

By forming we mean mechanical shaping operations normally requiring the application of a lubricant to the metal before or during a shaping operation, i.e. deformation by pressure against a solid surface. In particular the invention envisages plastic deformation of metallic materials both in the hot and in the cold. By the plastic deformation of metallic materials in the cold, we mean mechanical shaping operations applied to sheet, bar, wire and tubular materials such as, for example, the mechani-

cal shaping operations known as impact extrusion, spinning, drawing (including mandrel drawing, plug drawing and deep drawing), rolling, pressing and drop hammer forging. Deformation in the cold means that the metal itself is not deliberately heated to very high temperatures prior to deformation. It is sometimes desirable to warm up both the dies and coated metals to moderately elevated temperatures of the order of 50° C. to 100° C. prior to starting the initial forming operation. This can help in some cases to ease the initial forming operation until enough heat has been produced to soften the lubricant coating. If desired a small amount of a conventional lubricant such as oil or alternatively a chlorinated paraffin may be applied to the coated metal or to the tools to assist in the very early lubrication stages in the deformation treatment.

As organic solvent it is desirable to employ a major proportion of a non-inflammable chlorinated liquid, e.g. a chlorinated hydrocarbon such as trichloroethylene 1:1:1-trichloroethane, carbon tetrachloride, perchloroethylene, or methylene dichloride. A chlorofluorinated hydrocarbon such as trifluorotrchloroethane may be used. If desired small amounts of other organic solvents such as aliphatic or aromatic hydrocarbons, aliphatic or aromatic alcohols, esters or ketones may be admixed with the chlorinated solvent. We prefer to use trichloroethylene as the solvent in our compositions.

A wide variety of acrylic ester and methacrylic ester copolymers may be employed as the major film forming component of the coating composition, but the copolymer must contain a minor proportion of free carboxylic acid groups as the presence of such groups is found to increase the adhesion of the protective film to the metal. Suitable acrylic or methacrylic esters for use in preparing the copolymer are those obtained from aliphatic or cycloaliphatic alcohols containing not more than 18 carbon atoms preferably not more than 12 carbon atoms. If desired the ester monomers may be employed in admixture. Suitable unsaturated carboxylic acids may be for example acrylic acid, methacrylic acid, crotonic acid, maleic acid or fumaric acid. Mixtures of these acid monomers may be employed if desired. Minor proportions of other polymerisable monomers may also be included in the polymerisation mixture. We prefer to employ copolymers of methacrylic esters with methacrylic acid. Copolymers of β -ethoxy ethyl methacrylate with minor proportions of methacrylic acid are particularly suitable, for example a copolymer obtained from 98 parts by weight of β -ethoxy ethyl methacrylate and 2 parts by weight of methacrylic acid. Also quite suitable are copolymers of n-butyl methacrylate with minor proportions of methyl methacrylate and methacrylic acid for example a copolymer obtained from 88 parts by weight of n-butyl methacrylate, 10 parts by weight of methyl methacrylate and 2 parts by weight of methacrylic acid.

Suitable organic solvent soluble alkylated heat hardenable condensation products of formaldehyde with urea or melamine may be obtained by reacting a proportion of the methylol groups in a urea/formaldehyde or melamine/formaldehyde condensate with an alcohol for example an aliphatic alcohol such as n-butyl alcohol. Alternatively an alcohol, urea or melamine and formaldehyde may be reacted simultaneously to form the desired condensate.

As conventional lubricants there may be employed mineral lubricants such as graphite or molybdenum disulphide, mineral and vegetable oils, fats and waxes, and also synthetic lubricants such as chlorinated hydrocarbons and synthetic polymeric esters. Mineral oils are particularly useful as conventional lubricants.

In accordance with one aspect of the present invention, there is also used a chlorinated paraffin containing 20% to 30% by weight of chlorine. This material may be used alone or with any of the aforesaid lubricants.

Compositions containing this chlorinated paraffin give tough dry films possessing excellent adhesion to metal. With a chlorinated paraffin with a chlorine content of the order of 15% or less the addition of the chlorinated paraffin to the composition impedes solvent release and this leaves a coating on the metal which is quite wet and which possesses very little toughness or adhesion to metal. Surprisingly we have found at or above 20% chlorine this does not occur. However when the chlorine content of the paraffin exceeds 30% the coating begins to get tacky and at 35% the film produced begins to get very tacky and increasingly so as the chlorine content of the paraffin is increased. Preferably the chlorine content of the paraffin is 20% to 25%. Preferably also there is used a chlorinated paraffin prepared by chlorinating an essentially linear petroleum fraction having an average molecular weight in the range 144 to 562 and particularly a chlorinated paraffin wax obtained by chlorinating material having an average molecular weight in the range 282 to 366. I am aware that some chlorinated paraffins can be described as resins but the term resin as used in this specification does not include chlorinated paraffins.

The proportion of chlorinated paraffin in the coating composition (and hence in the film from which it is obtained) may be varied quite widely when the chlorine content is in the range 20% to 30%. It is possible to incorporate in the film as much as 55 parts of chlorinated paraffin wax to every 100 parts resin (or resin plus conventional lubricant) without getting a tacky film. It is preferred to form a film on the metal from a composition containing at least 10 parts but not more than 55 parts chlorinated paraffin wax, for example, 30 parts chlorinated paraffin wax to 100 parts resin (or resin plus conventional lubricant). A small amount of dyestuff may be added to the compositions of the present invention to aid in visual observation of the treated product.

For soft metals such as those composed mainly of aluminium, copper or brass it is often unnecessary to add the thermo hardening resin, lubricant or chlorinated paraffin to the coating composition possibly because less force is required to produce the shaped object and friction and heat generated during the shaping operation are also less than when hard metals are used.

For ferrous metals and particularly sheet steel the presence in the coating composition of minor proportions of thermo hardening component, lubricant and/or chlorinated paraffin is usually essential. For mild steel sheet preferred proportions of the ingredients, other than chlorinated hydrocarbon, present in the solution of the coating composition are:

	Percent by weight
Acrylic or methacrylic copolymer	50-98
Thermo hardening resin	1-20
Lubricant	1-35

In all the coating compositions of the present invention the acrylic and/or methacrylic copolymer comprises at least 30% by weight of the total matter dissolved in the organic solvent used for the coating composition, and preferably at least 50% by weight of the copolymer comprises an acrylic or methacrylic ester. When chlorinated paraffin is not used it is preferred to employ at least 50% by weight of acrylic and/or methacrylic polymer and generally that polymer is at least 50% of the components of the composition other than chlorinated paraffin. In most cases the thermo-hardening resin is not used with the chlorinated paraffin, but rather one or the other is employed.

The coating compositions may have a solids content of from 1.0% to 20% by weight.

The coating compositions are applied to the metallic articles by any convenient method, for example, by dip-

ping, brushing or spraying. The composition can if desired be heated to obtain faster production speeds. Thus, when using trichloroethylene as solvent, a hot dipping technique may be employed by heating the composition up to 87° C. Lower temperatures than 87° C. for example 50° C., may be employed in a partial hot dipping technique. The temperature will vary with different solvents used; the higher the boiling point of the solvent, the higher the temperature which may be used for hot-dipping. After the metal has been treated with the coating composition the chlorinated solvent is removed by evaporation at atmospheric temperature or at elevated temperature leaving a strongly adherent protective film.

Sheet metal coated with a protective film obtained by use of the coating compositions is extremely resistant to corrosion and damage due to mechanical causes. It thus provides a protective coating for metallic materials before being subjected to plastic deformation in the cold. In many cases the film remains intact after the completion of such deformation and in such cases serves to provide a protective coat for further deformation. The protective film is non-greasy, non-tacky, almost colourless and imperceptible to the touch. The addition of chlorinated paraffin to the composition gives an extremely adherent film even to very smooth metallic surfaces. It makes possible physical deformation without certain side effects such as fracturing or scoring for example, it permits better deep drawing of the hard metallic materials such as steel often without the requirement of or the very minimum of annealing between drawing stages. It provides better scratch protection and as the films are non-tacky the deformed articles may be packed without sticking and without collection of dust.

After the deformation treatment the film can easily be removed by conventional methods such as by heating in an annealing furnace (with a reducing atmosphere) or by degreasing techniques. The addition of a chlorinated paraffin to the composition does not result in the leaving of a residue after removal of the film.

The invention is illustrated but not limited by the following examples in which parts and percentages are by weight.

EXAMPLE 1

Part (a)

Sheet steel lubricated with conventionally known lubricants was pressed to form a castor bracket. After 250 pressing operations it was necessary to re-polish the tools. The pressings were also scratched and needed polishing.

Part (b)

When the sheet steel employed in Part (a) above was treated with a coating composition consisting of a 14% solution in trichloroethylene of a mixture of 4 parts of mineral oil and 10 parts of a copolymer obtained by polymerising 88 parts of n-butyl methacrylate, 10 parts of methyl methacrylate and 2 parts of methacrylic acid, 10,000 pressings free from tool marks were obtained before it became necessary to re-polish the tools.

EXAMPLE 2

Sheet aluminium alloy was treated with a coating composition consisting of a 10% solution in trichloroethylene of the copolymer employed in Part (b) Example 1. When pressed and formed there was no tool-marking of the alloy and the pressed objects were free from scratches. It was found that the use of any additional lubricant was unnecessary.

EXAMPLE 3

Part (a)

Sheet steel was being formed in four operations into a deep circular shaped pot. It was necessary to anneal

5

between each forming operation. Using a phosphate pretreatment and conventionally known lubricants in addition, splitting frequently occurred during the various forming operations and especially at the fourth operation.

Part (b)

When the sheet steel was coated with a composition consisting of a 10% solution in trichloroethylene of a mixture of 5 parts of the copolymer employed in Part (b) Example 1, 2½ parts of mineral oil and 1 part of a butylated ureaformaldehyde heat hardenable resinous condensate dissolved in 1 part of a mixture of butyl alcohol and xylene, it was possible to produce the pressings without splitting, to avoid the tool marking previously present, and to omit phosphate pretreatment. It was further possible to omit one or more annealing operations.

EXAMPLE 4

Part (a)

Sheet brass strip was pressed into a deep cup in four operations and with annealing between each pressing using conventionally known lubricants to avoid splitting caused by excessive heat and friction.

Part (b)

When the strip employed in Part (a) above was coated with a composition consisting of a 10% solution in trichloroethylene of the copolymer employed in Part (b) Example 1 the pressing could be made in one operation thereby cutting out the intermediate annealing and avoiding the tool marks that were previously present.

EXAMPLE 5

Circular blanks of stainless steel (18% Ni and 8% Cr) were treated with a composition according to the invention. A copolymer of β -ethoxy ethyl methacrylate with methacrylic acid in the proportion of 98 parts methacrylate to 2 parts of methacrylic acid was used. A chlorinated paraffin wax was obtained by chlorinating an essentially linear petroleum fraction having an average molecular weight in the range 282 to 366 so that the resulting chlorinated paraffin wax had a chlorine content of 25%. The copolymer was blended with 30% by weight of the chlorinated paraffin wax and with 30% by weight of a light mineral oil in trichloroethylene so that the solution contained 15% by weight of resin plus chlorinated wax plus oil.

The composition was applied by dipping the metallic material in the solution and withdrawing at a speed of 12 inches per minute. The solvent evaporated from the surface at ambient temperature and a film thickness of 0.0003 inch was thereby deposited. In other experiments the composition was warmed to 50° C. and a withdrawal speed of 2 ft./min. was used to provide a similar film thickness. In further experiment the concentration of the materials in the solvent was reduced to 10% and the composition was heated to 85° C. when a withdrawal speed of 4 ft./min. was used to give the desired film thickness which varied in the range 0.0002 to 0.0004 inch.

Coated blanks were then pressed in three separate stages, the first to give a cylinder 3⅞ inches deep and of diameter 5⅞ inches, then to a cylinder 4½ inches deep by 4½ inches diameter, and finally to a cylinder 5½ inches deep by 3¾ inches diameter. No intermediate annealing was required and only the original application of the composition was needed. No marks or defects were observed on the deformed metal surface.

Comparison.—By way of comparison stainless steel blanks as described in Example 5 were coated with a conventional lubricant based on heavy duty drawing oil loaded with talc and were pressed in 3 separate stages

6

to form cylindrical pots 5½ inches deep by 3¾ inches diameter. In contradistinction to Example 5 it was necessary to anneal between each operation and prior to the annealing the lubricant had to be removed and a fresh application had to be made prior to further drawing. The deformed metal had a scarred surface.

EXAMPLE 6

Blanks of lightly polished aluminium were treated with a composition in the same manner as in Example 5. The concentration of the material in trichloroethylene was varied and the withdrawal speed altered in accordance with this variation so as to give a film thickness in the range 0.0002 to 0.0004 inch. The blanks were then pressed in 3 stages and the films were removed by washing with trichloroethylene.

The surface remained undamaged. After the first drawing operation the lubricating film remained intact and in many cases a second operation could be effected without annealing. Experiments with brass, mild steel, a nickel alloy known under the registered trademark "Nimonic" 75, stainless steel, titanium and zirconium gave similar results.

Comparison.—By way of comparison similar aluminium blanks were coated with a conventional lubricant based on a heavy duty chlorinated mineral oil and containing talc and the metal was deformed once by deep drawing.

It was found that the metal surface had been scratched due to the action of the press tools.

EXAMPLE 7

A number of nickel/chromium alloy tubes, ½ inch, 1 inch, and 1⅞ inches in diameter were coated with the composition as described in Example 6.

The tubes were then plug drawn in two stages to give a reduction in surface area of 7½% with 22% reduction in wall thickness.

No intermediate annealing was required between the drawing stages. The tube was finally annealed but the lubricating film did not have to be removed as a separate operation since it volatilised or decomposed in the annealing furnace (having a reducing atmosphere) without deposition of a residue on the metal surface.

Comparison.—By way of comparison a similar nickel alloy tube was coated with a conventional type lubricant consisting of a sulphurised mineral oil and was plug drawn twice in the manner indicated in Example 7. An intermediate annealing was required and the lubricant had to be removed prior to annealing.

EXAMPLE 8

Unoxidised titanium tubes of diameter 1.6 inches, wall thickness 0.004 inch, were treated with the composition as described in Example 6. The tubes were then submitted to the following sequence of operations: plug drawn to a diameter of 1.44 inches and wall thickness 0.037 inch, annealed, plug drawn to diameter of 1.3 inches, wall thickness 0.034 inch, then without annealing plug-drawn to 1.17 inches, wall thickness 0.0315 inch, without annealing, plug drawn to 1.05 inches, wall thickness 0.029 inch, annealed, recoated, plug drawn to 0.945 inch, wall thickness 0.027 inch, plug-drawn without annealing to 0.850 inch, wall thickness 0.025 inch, plug-drawn without annealing to 0.765 inch, wall thickness 0.023 inch, annealed, recoated, plug-drawn to 0.688 inch, wall thickness 0.0215 inch, plug-drawn without annealing to 0.625 inch wall thickness 0.02 inch and finally annealed. The tubes were clean, bright and unmarked.

Comparison.—By way of comparison a titanium tube was coated with a heavy duty mineral oil containing calcium stearate and submitted to one plug-drawing. Severe pick-up occurred on the tube and lubrication was possible only if the metal was first oxidised.

EXAMPLE 9

The composition employed comprised 40 parts by weight of a copolymer of β -ethoxy ethyl methacrylate and methacrylic acid (in the proportion of 98 parts by weight methacrylate/2 parts acid), 16 parts by weight chlorinated paraffin wax (24% Cl_2) and 300 parts trichloroethylene. Stainless steel blanks were dipped into the coating composition maintained at 70–75° C. and were withdrawn at 3 feet per minute to give a film thickness of 0.0003 to 0.0004 inch.

The coated blanks were transformed into beakers 7 inches deep by 5 inches diameter in the following sequence of operations: first draw, second draw, third draw, anneal, stretch (to remove puckers), descale and lightly polish. The beakers were free from fractures and score marks and were of excellent surface appearance.

Comparison.—By way of comparison the stainless blanks were coated with a heavy duty mineral oil containing a sulphur-bearing compound and talc. The following sequence of operation was necessary to produce beakers of similar quality to those of Example 9: first draw, anneal, second draw, anneal, third draw, anneal, stretch, descale, heavy polish. The procedure of Example 9 at least saved two annealing operations.

EXAMPLE 10

Stainless steel sheet blanks were treated with a composition as in Example 9 except that the 40 parts of resin consisted of a copolymer of n-butyl methacrylate, methyl methacrylate and methacrylic acid (in the proportion by weight, respectively of 88:10:2).

The blanks were subjected to the following sequence of operations to produce sinks: press to 6 inches deep, press to 6½ inches deep, stretch to 7 inches deep, and lightly polish. The sinks were free from fractures or scores and of excellent surface appearance.

Comparison.—By way of comparison the stainless steel blanks were coated with a heavy duty mineral oil containing a sulphur-bearing compound and talc. The following sequence of operations were needed to produce sinks of similar quality to those of Example 10: press to 6 inches, anneal, descale, press to 6½ inches, stretch to 7 inches, heavy polish. Thus in Example 10 at least one annealing operation was saved.

The conventional lubricants used in Examples 1, 3 and 4 were heavy duty mineral oils containing talc and a chlorinated hydrocarbon.

What is claimed is:

1. A process for shaping metal which comprises subjecting to deformation by pressure against a solid surface metal which has been coated by applying to its surface a solution containing from about 1% to 20% by weight of a lubricating coating composition in an organic solvent and removing the solvent, said lubricating coating composition consisting essentially of a copolymer of at least one member of the group consisting of esters of acrylic acid and methacrylic acid together with a minor amount of an ethylenically-unsaturated carboxylic acid selected from the group consisting of acrylic, methacrylic, crotonic, maleic and fumaric acid, said carboxylic acid improving the adhesion of said copolymer to said metal.
2. A process as set forth in claim 1 in which the solvent is trichloroethylene.
3. A process as set forth in claim 1 in which the coating composition is a copolymer of n-butyl methacrylate with minor proportions of methyl methacrylate and methacrylic acid.
4. A process as set forth in claim 3 in which the coating composition is a copolymer of about 88 parts by weight n-butyl methacrylate, about 10 parts by weight methyl methacrylate and about 2 parts by weight methacrylic acid.
5. A process as set forth in claim 1 in which said esters are esters with aliphatic and cycloaliphatic alcohols containing not more than about 18 carbon atoms.

6. A process as set forth in claim 1 in which said solution also contains an organic solvent-soluble alkylated heat hardenable condensation product of formaldehyde and a member of the group consisting of urea and melamine, the amount of said condensation product being from 1% to about 20% by weight of said solids.

7. A process as set forth in claim 1 in which said solution contains from about 1% to 35% by weight of said composition of a mineral lubricant.

8. A process as set forth in claim 7 in which said mineral lubricant is graphite.

9. A process as set forth in claim 1 in which said solution contains from about 1% to 35% by weight of said composition of an oily lubricant.

10. A process as set forth in claim 9 in which said oily lubricant is mineral oil.

11. A process for shaping metal which comprises subjecting to deformation by pressure against a solid surface metal which has been coated by applying to its surface a solution containing from about 1% to 20% by weight of a lubricating coating composition in an organic solvent and removing the solvent, said lubricating coating composition consisting essentially of a copolymer of at least one member of the group consisting of esters of acrylic acid and methacrylic acid together with a minor amount of an ethylenically-unsaturated carboxylic acid selected from the group consisting of acrylic, methacrylic, crotonic, maleic and fumaric acid, said carboxylic acid improving the adhesion of said copolymer to said metal, and a chlorinated paraffin of chlorine content in the range 20% to 30% by weight, said chlorinated paraffin being present in an amount from about 10 to 55 parts per 100 parts of said copolymer.

12. A process as set forth in claim 11 in which the chlorinated paraffin employed is a chlorinated paraffin wax of chlorine content 20% to 25% by weight.

13. A process as set forth in claim 11 in which the chlorinated paraffin is obtained by chlorinating an essentially linear petroleum fraction having an average molecular weight in the range 114 to 562.

14. A process as set forth in claim 13 in which the average molecular weight of said linear petroleum fraction is in the range 282 to 366.

15. A process as set forth in claim 11 in which said solvent is trichloroethylene.

16. A process as set forth in claim 11 in which said esters are esters with aliphatic and cycloaliphatic alcohols containing not more than about 18 carbon atoms.

17. A process as set forth in claim 11 in which the copolymer is a copolymer of methacrylic acid with an ester of methacrylic acid.

18. A process as set forth in claim 11 in which said copolymer comprises at least about 30% of said lubricating coating composition.

19. A process as claimed in claim 1 in which the coating composition is heated before application to the metal.

20. A solution of a lubricating coating composition, useful for application to a metal to aid in plastic deformation thereof, which comprises a solution in an organic solvent containing from about 1% to 20% by weight of a lubricating coating composition of (1) a copolymer of at least one member of the group consisting of esters of acrylic acid and methacrylic acid together with a minor amount of an ethylenically-unsaturated carboxylic acid selected from the group consisting of acrylic, methacrylic, crotonic, maleic and fumaric acid, and (2) a chlorinated paraffin of chlorine content in the range 20% to 30% by weight, said chlorinated paraffin being present in an amount from about 10 to 55 parts per 100 parts of said copolymer.

21. A solution of a coating composition as set forth in claim 20 in which the chlorinated paraffin employed is a chlorinated paraffin wax of chlorine content 20% to 25% by weight.

22. A solution of a coating composition as set forth in claim 20 in which the chlorinated paraffin is obtained by

9

chlorinating an essentially linear petroleum fraction having an average molecular weight in the range 114 to 562.

23. A solution of a coating composition as set forth in claim 22 in which the average molecular weight of said petroleum fraction is in the range 282 to 366.

24. A solution of a coating composition as set forth in claim 20 in which said esters are esters with aliphatic or cycloaliphatic alcohols of not more than about 18 carbon atoms.

25. A solution of a coating composition as set forth in claim 20 in which the copolymer is a copolymer of methacrylic acid with an ester of methacrylic acid.

26. A solution of a coating composition as set forth in claim 20 in which said copolymer comprises at least about 30% of the said lubricating coating composition.

27. A coating composition as set forth in claim 26 which contains 10 to 55 parts of chlorinated paraffin to 100 parts of said copolymer.

10

References Cited by the Examiner

UNITED STATES PATENTS

2,345,198	3/1944	Hodson	252—22
2,346,124	4/1944	Dew	252—33.4 X
2,529,188	11/1950	Rocchini et al.	252—58
2,588,234	3/1952	Hendricks	252—18 X
2,787,603	4/1957	Sanders	117—132 X
3,037,955	6/1962	Carman	117—132 X

FOREIGN PATENTS

769,427 3/1957 Great Britain.

OTHER REFERENCES

15 "Chemical and Engineering News," vol. 31 (1953), page 236, "Trichloroethylene," Shepard.

DANIEL E. WYMAN, *Primary Examiner*.

W. H. CANNON, *Assistant Examiner*.