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(71) Applicant: **CENTRO SVILUPPO MATERIALI S.p.A.**
Via di Castel Romano 100-102
I-00129 Roma(IT)
Applicant: **LUBRITALIA S.p.A.**
Zona Industriale
Località Marco dei Lupini
Scalo FF.SS.
I-74019 Palagiano Taranto(IT)

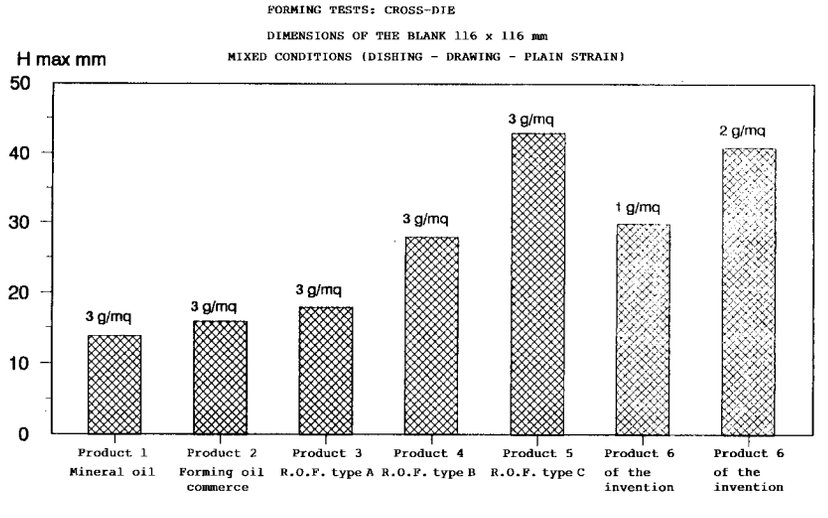
(72) Inventor: **Colaiacovo, Ferdinando**
Via Leonardo Greppi no. 77
Rome(IT)
Inventor: **Granata, Francesco**
Via Marco Basile Case Nuove
Palagiano Taranto(IT)

(74) Representative: **Klausner, Erich et al**
c/o Ufficio Internazionale Brevetti
Ing. C. Gregorj S.p.A.
Via Dogana 1
I-20123 Milano (IT)

(54) **A synthetic, mineral oil free, forming oil composition dispersed in a hydroalcoholic medium.**

(57) Described is a forming oil composition, on synthetic basis, free from mineral oils, dispersed in a hydroalcoholic medium. Said forming oil can be applied by spraying, rolling or immersion, or other convenient methods, be it directly on coils, be it in the forming department. After drying, the forming oil yields a removable organic film (R.O.F.).

FIG. 3



LUBRICATING POWER OF THE INVENTIVE COMPOSITION OVER OTHER COMMERCIAL R.O.F. COMPOSITIONS

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The instant invention concerns a lubricating agent, viz. a forming oil, on synthetic basis, free from mineral oils, dispersed in an aqueous vehicle, having high lubricity and protective characteristics, particularly indicated for forming operations, even extreme ones. More particularly, the instant invention concerns a forming oil, on synthetic basis, free from mineral oils, formulated in the form of a hydroalcoholic dispersion, which can be applied by spraying, rolling or immersion, or by any other convenient method, be it directly on coils, at the exit of the production lines provided with a coating-drying section (at a temperature of approx.60 °C) before the winding of the coil, or in the forming department. After drying, there remains on the steel sheet a "quasi solid" organic film capable of ensuring a very high lubricity which helps to avoid those phenomena which could lead to surface fouls (such as e.g. scratches, accumulation of dirt, pittings) which occur especially with electro-galvanized sheet steel.

When forming sheet steel, mainly in the automotive industry, mineral lubricants are usually employed. The sheet steel manufactured in steel mills is protected by protective oils which also act as forming oils in less severe forming operations.

For heavy-duty operations, in the forming departments, the sheet steel is further lubricated, off-press (manually or automatically) or in the press, with more viscous oils having higher lubricity.

In the 70s, synthetic forming oils were developed, mainly on the basis of acrylic polymers, in a solvent medium, or dispersed in an aqueous medium, which after drying or thermal curing yield solid films on the metal surface; such synthetic forming oils, when applied in an amount of 3-4 g/m^2, develop lubricities comparable or superior to the best oil lubricants.

Nonetheless, said polymeric products require plants of coating and drying, or of curing at high temperature (160 ° to 220 °C) which, for economical reasons, can only be employed in sheet steel mills. The thus pre-lubricated sheets can be formed on the user's site without additional lubricating operations, to the great advantage of industrial hygiene,the handling and dripping of mineral oils being avoided. But these forming oils have not yet encountered wide-spread use, mainly for the following reasons:

- higher initial cost of the pre-lubricated sheet steel;
- problems linked to the minimum effective coating thickness to be applied (3/4 g/m^2);
- spot welding problems due to too high an electrical insulation, and to fume development (from the burnt lubricant);
- difficulties in removing the coated areas during the degreasing step prior to phosphating and/or painting the formed articles;

furthermore, the prior art water-soluble or water-dispersible lubricating materials normally have a lower rust-inhibiting power, particularly on uncoated sheet steel, than that of mineral oil protective lubricants, this because of their higher hygroscopicity.

The increased use of coated sheet steel, especially electro-galvanized sheet steel, which involves more problems in the forming step (higher degree of friction, formation of dirt deposits and pittings)as well as greater attention to industrial hygiene problems and to the disposal of industrial wastes, make the necessity of replacing mineral oils by more effective and less polluting lubricating materials a more relevant issue.

In the light of this, applicants have developed a new type of material, on a synthetic basis, dispersed in an aqueous vehicle, capable of forming a removable organic film (R.O.F.) which amply overcomes the drawbacks which up to now have restricted the diffusion of materials on a polymer basis as an alternative to mineral oils.

The lubricating material of the instant invention offers in fact the following advantages:

- lower cost,
- lower effective R.O.F. thickness, by at least 30%, in the forming step,
- the protective R.O.F. does not suffer brittleness or peeling even in the most stressed zones,
- no need for thermal curing of the R.O.F.,
- absence of acrylic polymers, mineral and aromatic solvents,
- absence of harmful and/or unpleasant fumes in the drying step,
- improved removability of the protective R.O.F., be it over the prior art polymeric film-forming lubricants, be it over the mineral oil lubricants,
- ensured complete removability of the R.O.F., even in the zones exposed to fumes coming from structural adhesives,
- compatibility with the structural adhesives usually employed in the automotive industry,
- excellent electric weldability due to a higher conductivity of the lubricating film,
- biodegradability, in tanks containing activated sludge.

As regards the above mentioned lower cost, let it be pointed out that this is due to the following factors. In the first place, the use of the inventive lubricanting material no longer demands additional lubricating steps, in the press or off-press, from which ensues saving lubricant, manpower, and reduction of working

time.

Moreover, the use of the inventive lubricating material allows to considerably reduce manufacturing wastes and to use cheaper sheet steel, i.e. having lower forming characteristics.

As far as the investment and power costs are concerned, these - at a first estimate - for a coating and drying plant, are of the same order as those of electro-static oiling plants using materials on a mineral basis.

The cost impact of the synthetic forming oil is instead linked to the minimum effective thickness for achieving lubrication, as it can be taken from the histogram in Fig.1.

The inventive lubricating material, because of its particular adjuvants and coatability, allows to obtain an excellent protection even of the formed parts having mechanically severely stressed zones. In an accelerated corrosion test with formed articles kept in a climatic chamber for one month at 40 °C, with 85% relative humidity (R.H.), no red-rust focuses are detectable.

The inventive forming oil exhibits superior (approx. double)lubricity vis-à-vis the mineral oil materials already at coating weights of 1 g/m^2. The lubricity increases further in asymptotic manner at coating weights of 2-3 g/m^2.

The lubricity characteristics are excellent be it under prevailing dishing working conditions,be it under mixed conditions (viz. dishing, drawing, plane strain).

The results of the qualification tests are given in the histograms of Figures 2 and 3.

Furthermore,the improved electrical conductivity of the forming oil of the instant invention allows to weld in the presence of protective films having coating weights greater than 3 g/m^2,not possible with other materials on a polymer basis. The graphs in Fig.4 illustrate comparatively the different materials.

The removability and phosphatability have been assessed by simulating the degreasing and phosphating operations typical of the automotive industry.

The excellent removability and subsequent phosphatability of the material have been shown even on protected zones, which have been simulated by the juxtaposition of the steel plates with an interspace of approx. 100 μm, as shown by the diassembled sample illustrated in Fig.5.

The mechanical resistance of the joints obtained with the use of structural adhesives, of the epoxide resin/PVC type, used in the automotive industry, is not affected by the presence on the steel sheets of the inventive lubricant, up to an amount of 5 g/m^2.

As to the fouling of the degreasing baths, lab tests have shown that progressive additions (up to a 1:1 ratio) of the inventive lubricant to the alkaline degreasing bath does not affect its degreasing capability.

As to the biodegradability of the inventive composition, it has been ascertained that aqueous solutions containing 5 g/l of said composition have a BOD5 of 735 mg/l of oxygen.

The inventive forming oil can be applied substantially in three different modes:

1) At the exit of the continuous lines (skin-pass,pickling, zinc plating) by means of a coating roll (oiler) or by percolating on the upper face of the sheet steel and subsequent dosing by means e.g. of doctor rolls or blades; whereupon the composition is partially air-dried at 50 ° to 80 °C, after which the thus treated sheet steel is coiled.

2) By means of dosing devices located at the exit of the unit where the steel coil is levelled and cut into sheets and subsequently partially air-dried at 50 ° to 80 °C.

3) Immediately prior to the forming operation, by using commercially available oiling/dosing machines, or in a spray cabin, on the cut sheet steel. In this case it is advisable that the lubricant material should have a flow-ability of from 16 to 60 cSt.

The inventive lubricating material consists of a mixture of products (components)dispersible in a hydroalcoholic medium selected from the hereinafter listed classes of products.

PRODUCTS OF CLASS 1

These are substances acting predominantly as greasing/lubricating agents, soluble/dispersible in a hydroalcoholic solution; said substances consist of ethoxylated (5-15 ethoxide(EtO) groups) fatty amines and fatty amides (C_{12}-C_{25}). Specific examples of substances of this class, useful for making the inventive lubricant,are:polyoxyethylene-(5)-dodecaneamine,bis-2-hydroxyethyl-oleilamine, polyoxyethylene-(5)-oleilamine,bis(2-hydroxyethyl)-tallow amine, polyoxyethylene-(5-ethoxy)-tallow amine, polyoxyethylene-(15-ethoxy)-tallow amine, N,N,N-tris-2-hydroxyethyl-N-tallow-1,3-diaminepropane, coconut monoethaneamide with 6 EtO groups, oleic acid monoethanolamide with 8 EtO groups, stearic acid monoethanolamide with 8 EtO groups.

Other useful products of this first class consist of saltified derivatives of imidazoline, such as e.g. 1-methyl-2-alkyl-3-metasulfate-amidoethylimidazoline (wherein "alkyl" is a C_9H_{17} and/or $C_{11}H_{21}$ group), 2-alkyl-1-oxyethyl-2-imidazoline saltified with sodium monochloroacetate.

Furthermore, according to the instant invention, as products of Class 1 can also be used derivatives of saltified amines and amides, such as e.g. castor oil propylamidotrimethylamine methylsulfate, methyl-bis-(tallow-amidoethyl)-2-hydroxyethylammonium methylsulfate, lauric acid pentoxymethylamine methylsulfate, (dicarboxylic acid isopropyl ester) dimethylamine methylsulfate: commercially known as REWOQUAT CR 3099 (Schering S.p.A., Segrate,Milano,Italy).

Also ethylene or (75/25) ethylene/propylene polyglycols, having m.w. of from 200 to 30,000, can be usefully employed for making the inventive forming oil. Illustrative examples of such compounds are e.g.: polyethylene glycols having m.w. of from 200 to 4,000, polyglycols (50/50 ethylene/propylene), having a viscosity (40 °C) of from 10 to 1,000 cSt, polyglycols (75/25 ethylene/propylene), having a viscosity (40 °C)- of from 270 to 30,000 cSt. Still other useful products of this class consist of monoesters and monoethers of polyglycols, such as e.g. PEG 200/400 monolaureate, PEG (200/600) monolaureate, PEG (200/600) monostereate, polyoxyethyleneglycol (1,000) monocetylether.

Finally, lanolin and derivatives thereof, such as e.g. lanolin sulfosuccinate, with 5 ethoxy groups, can be used.

PRODUCTS OF CLASS 2

These are high molecular weight substances,soluble/dispersible in hyroalcoholic solutions, acting predominantly as film-forming/lubricating agents.To begin with can be cited polyvinylpyrrolidone and copolymers thereof, such as e.g. PVP, having m.w. of from 2,500 to 2,800,000, PVP/VA E 735 (70/30), PVP/VA E 355 (30/70); wherein PVP stands for polyvinylpyrrolidone and VA stands for vinyl alcohol. Also polyvinyl alcohols and copolymers thereof, such as PVA-hydrolyzates (80-100%) are useful for the invention.

Further, also polyvinyl acetate-carboxylate copolymers, such as e.g. the vinyl acetate and crotonic acid 1:1 copolymers, per se or neutralized with 2-amino-2-methyl-1,3-propanediol, are compounds having mainly film-forming activity.

Also methylvinyl ether copolymers, such as e.g.methylvinyl ether maleic anhydride in a 1 : 3.3 : 1 ratio, neutralized with 1-amino-2-methyl-1,3-propanediol, can be advantageously used for the invention.

Moreover can be employed also dispersions of acrylic polymers, having m.w. of from 6,000 to 11,000, such as e.g. a 25-45% acrylic resin, like JONCRYL 678, of Chem Plast S.p.A. Milano, Italy, or DICRYLAN 325, of Ciba Chemical.

Also copolymers of methylvinyl ether maleic anhydride are compounds having film-forming/lubricating activity useful for the invention. Amongst these can be cited, e.g. the commercial products CONTREY ES 425 and ES 225 of Ciba Chemical, in (50%) alcoholic solutions and neutralized with triisopropanolamine.

Further, also tall oil rosin acids can be used, a typical commercially available representative of which is UNITOL NCY (manufactured by Union CAMP.Chemical and sold by CHEM-Verga, Rome, Italy). Also cellulose ethers, such as e.g. methylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose can be used. Typical commercial representatives are e.g. CELLOSIZE QP 300 H and QP 52,000 H, CELLOCOND 400 A and 100,000 A (Chem Plast S.p.A.,Milano, Italy), METHOXEL A and K (Dow-Chemical, U.S.A.).

Higher (C_{12}-C_{22}) fatty alcohols are also useful as components having film-forming/lubricating activity. Amongst the latter, merely as an illustrating example, can be cited: cetyl alcohol, stearic alcohol.

Finally, can be cited paraffin and polyethylene waxes, such as e.g. JONWAX 120 and JONWAX 35, AQUA POLYSILK 19,AQUA POLYFLUO 411 (Chem Plast S.p.A.,Milano, Italy).

PRODUCTS OF CLASS 3

These are substances acting predominantly as anti-corrosion and lubricating agents, soluble/dispersible in alcoholic solutions. Typically, these substances can consist of mixtures of straight and branched chain dicarboxylic and monocarboxylic acids saltified with an alcanolamine, such as e.g.a mono-, di-, tri-ethanolamine; an isopropylamine or a dibutylamine (at pH 8-10) or with soda (at pH 10-12).

The straight and branched chain monocarboxylic fatty acids of the above referred mixtures are acids having 8 to 22 carbon atoms in their molecule, such as e.g. capric, lauric, beenic acid or mixtures of predominantly unsaturated fatty acids, such as e.g. oleic,palmitoleic, linoleic, linolenic, erucic acid or tall oil rosin acids and tallow fatty acids.

The dicarboxylic acids of the above referred mixtures consist e.g. of dodecenylsuccinic and sebacic acid, and mixtures of dimer acids, such as e.g. a dimer acid made by polymerizing an unsaturated fatty acid, having 18 carbon atoms, and containing of from approx. 80 to 97% dimer acid, of from approx. 20 to 3% trimer acid and a maximum of approx. 1.1% monomeric acid. Typically, approx. 95% dioleic acid,

approx. 4% trimer acid and approx. 1% monomeric acid. Such an acid has an AN (acidity number) of approx. 191, a combining equivalent of approx. 293 and a m.w. of approx.365.

Dimer acids corresponding to the above referred characteristics are commercially available, e.g. under the trade-name PRIPOL from Unichema International.

Also water dispersible alcanolamides of the oleic acid, such as e.g. hydroxyoleilamide, can advantageously be employed.

PRODUCTS OF CLASS 4

As indicated in the introductory part, the forming oil compositions of the instant invention are formulated in a hydroalcoholic medium; useful alcohols are, e.g., the following: ethyl, isopropyl, cyclohexyl, butylcellosolve or also materials consisting of a monoalkylether of an alkyleneglycol of formula

$$R_1O[CH_2C(R_2)OH]_yOH$$

wherein

R_1 is a (C_1-C_4) alkyl and

R_2 is H, or -CH_3, and

y is an integer from 1 to 3.

At present,preferred glycol ethers are selected from 2-ethyl-1,3-hexanediol/ethyleneglycol in a 3:1 molar ratio and the like.

As it is known to the skilled artisans, for making lubricating compositions in general, for various reasons pure starting materials are not used but rather so-called technical materials which contain, even in substantial amounts, by-products or impurities stemming from the manufacturing process thereof.

Thus, e.g., when reference is made to "fatty acids", in the majority of cases implied is not a single acid but rather an acid mixture, the main component of which can be present even in concentrations "as low" as 60-70%. This applies to the materials in all the above referred four classes.

Further, it is pointed out that not all the mentioned materials are directly soluble or dispersible in an aqueous or hydroalcoholic medium, in which case - as it is known to the skilled artisan - it will suffice to resort to the aid of wetting or emulsifying agents. Such agents are widely known in the art and technical literature and easily available on the market. Also the manner of using said agents is widely known and, thus, there is no need to ballasting the present specification by describing them and/or illustrating their mode of use.

The invention will now be better illustrated by way of the following examples.

Example 1

This example describes the preparation of a forming oil of the invention, consisting of the following components:

- a branched chain (C_8) monocarboxylic acid: 2,2-dimethylhexanoic acid, saltified with triethanolamine up to pH 9-10;
  concentration: 2-4%;
- a tall oil rosin acid (such as e.g.UNITOL NCY),saltified with 10%NaOH, in a hydroalcoholic solution (50% isopropyl alcohol);
  concentration: 1-5%;
- a 35% PVA copolymer dispersion (such as e.g. OPTAFIX PAF 35 from Zschimmer-Schwarz GmbH, Germany);
  concentration: 1-5%
- a polyoxyethylene (5 EtO) oleilamine,
  concentration: 7-14%;
- a hydroalcoholic solution (10% ethyl alcohol) q.s. to 100 ml.

Standard Preparation

To the amount of water required for the formulation are added monocarboxylic acid and triethanolamine in a 1:1 molar ratio; the reaction mixture is stirred up to a clear solution. In the first stage the temperature is maintained at 50 °C; after dissolution, if necessary, the pH is adjusted to 9-10 by supplemental addition of triethanolamine.

Then is added a tallow rosin acid presaltified as follows:

demineralized water	44%
isopropyl alcohol	44%
sodium hydroxide	2%
UNITOL NCY	10%.

First the sodium hydroxide is dissolved in the hydroalcoholic medium, whereupon UNITOL NCY is added under vigorous stirring up to complete dissolution.

Then, under constant stirring and at ambient temperature are added, in the following order, the 35% PVA copolymers, the polyoxyethylene oleilamine and ethanol, in the amounts provided for.

Example 2

Another forming oil composition of the invention can be prepared using the following components:

- a dicarboxylic acid prepared by polymerizing a(C_{18}) unsaturated fatty acid, containing 80-97% dimer acid, 3-20% trimer acid and ≦ 1% monomer acid (such as e.g. PRIPOL 1022, Unichema Int'l), saltified with an isopropanolamine to pH 9-10,
  concentration: 2-5%;
- CELLOSIZE HEC 4400 (Union Carbide),
  concentration: 1-2%;
- a quaternary derivative of imidazole:1-methyl-2-alkyl-3-metasulfate-amidoethylimidazoline (such as e.g. REWOQUAT W7500, Rewo Chemische Werke),
  concentration: 5-10%;
- a hydroalcoholic solution (10% ethanol) q.s.to 100 ml.

Standard Preparation

To the amount of water required for the formulation are added dicarboxylic acid and isopropanolamine in a 1:2 molar ratio; the reaction mixture is maintained at 60 °C under stirring, up to complete dissolution of the acid; the pH is adjusted to 9-10, if necessary, by further adding isorpopanolamine.

At this point in time, after having lowered the temperature to ambient and under constant stirring, the other components, as listed hereinabove, are added, ethanol included.

Example 3

The inventive forming oil can also be made up as follows:

- a hydrogenated dimer acid, having an acid number of approx. 193 mg KOH/g and an equivalent weight of approx.90 and an iodine number of approx. 30 (such as e.g. REOCOR 190, Ciba Geigy) in a 1:1 mixture with(C_{18}-C_{22})straight-chain saturated fatty acids,saltified with diethanolamine to pH 9,
  concentration: 15-25%;
  CONTREY ES 425 and ES 225 (Ciba-Geigy), in a 50% alcoholic solution and neutralized with triisopropanolamine;
  concentration: 3-5%;
- PE/paraffin wax emulsified with cationic surfactants at pH 8.3 in a 30-40% concentration (such as e.g. JONAWAX 120-SC, Johnson Wax)
  concentration: 25-35%;
- a hydroalcoholic solution (2% butylcellosolve) q.s. to 100 ml.

Standard Preparation

To the hydroalcoholic medium required for the formulation are added the acid components and the diethanolamine in a 1:1 molar ratio.

The reaction mixture is well stirred, at 60 °C, up to complete dissolution of the acid component; the pH is adjusted to 9, if necessary, by further adding diethanolamine.

All the other above listed components are then added under constant stirring, at ambient temperature.

Example 4

An inventive forming oil composition can also be prepared using the following components:

- a mixture of linear(C_{12}-C_{18})monocarboxylic acids saltified with triethanolamine to pH 8, concentration: 1-5%;
- a lanolin polyglycol ether sulfosuccinate (40% solids) (such as e.g. REWOLAN 5, Rewo Chemische Werke), concentration: 1-5%;
- a polyvinyl alcohol hydrolizate (87-89%) (such as e.g. OPTAFIX PA 4 G,Zschimmer-Schwarz GmbH), concentration: 4-7%;
- a ricinoleylpropylamidotriethylamine methylsulfate, concentration: 7-14%;
- a hydroalcoholic solution (5% butylcellosolve) q.s. to 100 ml.

Standard Preparation

To the hydroalcoholic medium required for the formulation is added the mixture of the linear monocarboxylic acids and triethanolamine in a 1:1 molar ratio. The reaction mixture is kept under good stirring, at 60 °C, up to complete dissolution of the acid component; the pH is adjusted to 8, if necessary, by further adding triethanolamine.

The temperature is lowered to ambient and all the other above listed components are added under constant stirring.

Example 5

According to the instant invention, a forming oil is also made up as follows:

- a triethanolamine dodecenylsuccinate, concentration: 1.5-2%;
- a polyvinylpyrrolidone having a mean m.w. of 55,000, concentration: 5-10%;
- a stearic acid monoethanolamide having 8 ethoxy groups, concentration: 2-10%;
- perhydrosqualene, concentration: 0.1-0.5%;
- a hydroalcoholic solution (10% ethanol) q.s. to 100 ml.

Standard Preparation

All the above listed components required for the formulation are added to the hydroalcoholic medium at ambient temperature and under good stirring.

Example 6

Another lubricating formulation according to the invention is the following:

- polyoxyethylene dedocanoamine (5 EtO), concentration: 5-10%;
- ethanol, concentration: 1-2%;
- an acrylic resin (such as e.g. JONCRYL 678,Chem Plast, Milano) solubilized as follows:

water	52.1%
isopropanol	3%
propyleneglycol	1.5%
acrylic resin	35%
ammonia	8.4%;

to the water, heated at 80-90 °C,isopropanol and propyleneglycol are added, whereupon, under vigorous stirring, the acrylic resin and subsequently ammonia are added, concentration: 3-5%;

- a mixture of amine salts of fatty acids and butylammonium caprilate, concentration: 1-3%;
- a hydroalcoholic solution on the basis of 2-ethyl-1,3-hexanediol (30%), q.s. to 100 ml.

Standard Preparation

To the hydroalcoholic medium required for the formulation are added, under good stirring and at ambient temperature, all the above listed components; the JONCRYL 678 resin, solubilized as indicated above, is added last.

In Fig.6 are compared the properties of the exemplified lubricating materials disclosed in Examples 1-6, as resulting from the tests carried out in the laboratory and,with reference to the formulation of Examples 1 and 3, as resulting from industrial scale tests wherefor the formulation of Example 1 has been used for forming unprotected steel for bath tubs; the formulation of Example 3 instead has been used for forming electro-galvanzied sheet steel for panels for the automotive industry.

The rating is expressed on the basis of a 1 to 5 grade scale, wherein 1 indicates the worst rating and 5 the best. EXPLANATORY NOTES ON THE PRODUCTS REFERRED TO IN FIG.3.

Product 1 : A protective mineral oil with an antirust additive, viscosity at 40 °C = 22.1 cSt.

Product 2 : A forming mineral oil with polar additives, viscosity at 40 ° = 157 cSt.

Products 3-4 (R.O.F.type A-B resp.) : Solid films, obtained by drying at 80-100 °C, sheet steel coated with commercial products on the basis of acqueous dispersions of acrylic polymers. (also quoted as Products

Product 5 (R.O.F.type C resp.) : A solid film obtained by drying at 200 °C, sheet steel coated with a commercial product on the basis of curable modified acrylic resins.

Product 6 : A semi-solid film obtained by drying at 60 °C, sheet steel coated with the inventive forming oil of Example 1.

Claims

1. A synthetic, mineral-oil-free, forming oil composition, characterized by the fact that said composition comprises:

a) at least one substance acting predominantly as a greasing and lubricating agent, soluble or dispersible in a hydroalcoholic medium;

b) at least one high molecular weight substance acting predominantly as a film-forming and lubricating agent, soluble or dispersible in a hydroalcoholic medium;

c) at least one substance acting predominantly as an anti-corrosion and lubricating agent, soluble or dispersible in a hydroalcoholic medium;

d) an alcohol or a material consisting of a mono(lower)alkyl ether and an alkylene glycol;

e) water.

2. A forming oil composition according to claim 1, characterized by the fact that:

a) the substance acting predominantly as a greasing and lubricating agent comprises:

i) an ethoxylated fatty amine or fatty amide, having of from 12 to 25 carbon atoms and of from 5 to 15 ethoxide groups in its molecule, or

ii) a saltified amine or amide, or

iii) a saltified imidazoline derivative, or

iv) an ethylene or a (75/25) ethylene/propylene polyglycol having a molecular weight of from 200 to 30,000, or
v) a polyglycol monoester or monoether, or
vi) lanolin or a derivative thereof;

b) the high molecular weight substance acting predominantly as a film-forming and lubricating agent is selected among at least one of the following groups of compounds:
i) polyvinylpyrrolidone and copolymers thereof, or
ii) polyvinyl acetate-carboxylate copolymers, or
iii) methylvinyl ether copolymers, or
iv) dispersions of acrylic polymers, having a molecular weight of from 6,000 to 11,000, or
v) methylvinyl ether/maleic anhydride copolymers,or
vi) tall oil rosin acids, or
vii) cellulose ethers, or
viii) (C_{12}-C_{22}) fatty alcohols, or
ix) paraffin and polyethylene waxes;

c) the substance acting predominantly as anti-corrosion and lubricating agent comprises:
i) a mixture of straight or branched chain dicarboxylic and monocarboxylic acids saltified either with alcanolamine,at pH 8-10, or with sodium hydroxide, at pH 10-12, or
ii) an oleic acid alcanolamide;

d) an alcohol or a compound of formula

$R_1O[CH_2C(R_2)OH]yOH$

wherein R_1 is a (C_1-C_4) alkyl group, R_2 is hydrogen or -CH_3, and y is an integer of from 1 to 3.

3. A forming oil composition according to claim 1, characterized in that it comprises:
a) 2-4% of 2,2-dimethylesanoic acid, saltified with triethanolamine, at pH 9-10;
b) 1-5% tall oil rosin acids saltified with 10% NaOH in a 1:1 water/isopropyl alcohol medium;
c) 1-3% of a 35% PVA copolymer dispersion;
d) 7-14% polyoxyethylene oleilamine, wherein the polyoxyethylene contains 5 ethoxide groups;
e) an amount of a 90:10 water/ethanol medium sufficient to 100 parts (volume).

4. A forming oil composition according to claim 1, characterized by the fact that it comprises:
a) 2-5% of a carboxylic acid prepared by polymerizing a (C_{18}) unsaturated fatty acid, containing 80-97% dimer acid, 3-20% trimer acid and a maximum of 1% monomer acid, saltified with isopropanolamine, at pH 9-10;
b) 1-2% of a cellulose ether;
c) 5-10% of 1-methyl-2-alkyl-3-metasulfatoamido ethylimidazoline;
d) an amount of a 90:10 water/ethanol medium sufficient to 100 parts (volume).

5. A forming oil composition according to claim 1, characterized in that it comprises:
a) 15-25% of a hydrogenated dimer acid, having an acid number of approx. 193 mg KOH/g, a combining equivalent of approx. 90, and an iodine number of approx. 30, in a 1:1 mixture with linear saturated (C_{18}-C_{22}) fatty acids, saltified with diethanolamine, at pH 9;
b) 3-5% of CONTREY ES 425 and ES 225, in a 50% hydroalcoholic solution, neutralized with triisopropanolamine;
c) 25-35% of a PE/paraffin wax, emulsified with cationic tensides, at pH 8.3, at approx. 30-40% concentration;
d) an amount of a 95:5 water/butylcellolosolve medium sufficient to 100 parts (volume).

6. A forming oil composition according to claim 1, characterized in that it comprises:
a) 1-5% of a mixture of (C_{12}-C_{18}) monocarboxylic acid, saltified with triethanolamine, at pH 8;
b) 1-5% lanolin polyglycol ether sulfosuccinate, with a 40% solids content;
c) 4-7% of an 87-89% hydrolizate of polyvinyl alcohol;
d) 7-14% of ricinoleylpropylamidotriethylamine methylsulfate;
e) an amount of a 95:5 water/butylcellosolve medium sufficient to 100 parts (volume).

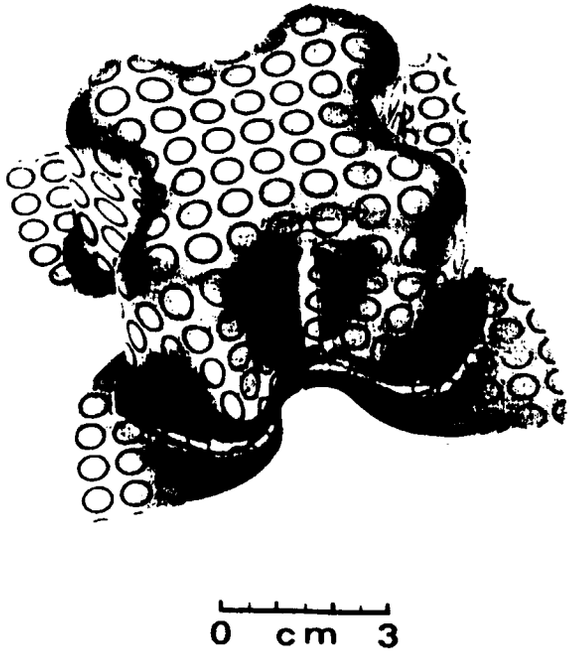
7. A forming oil composition according to claim 1, characterized in that it comprises:

a) 1.5-2% triethanolamine dodecylsuccinate;
b) 5-10% polyvinylpyrrolidone having a mean molecular weight of 55,000;
c) 2-10% stearic acid monoethanolamide, containing 8 ethoxide groups in the molecule;
d) 0.1-0.5% perhydrosqualene;
e) an amount of a 90:10 water/ethanol medium sufficient to 100 parts (volume).

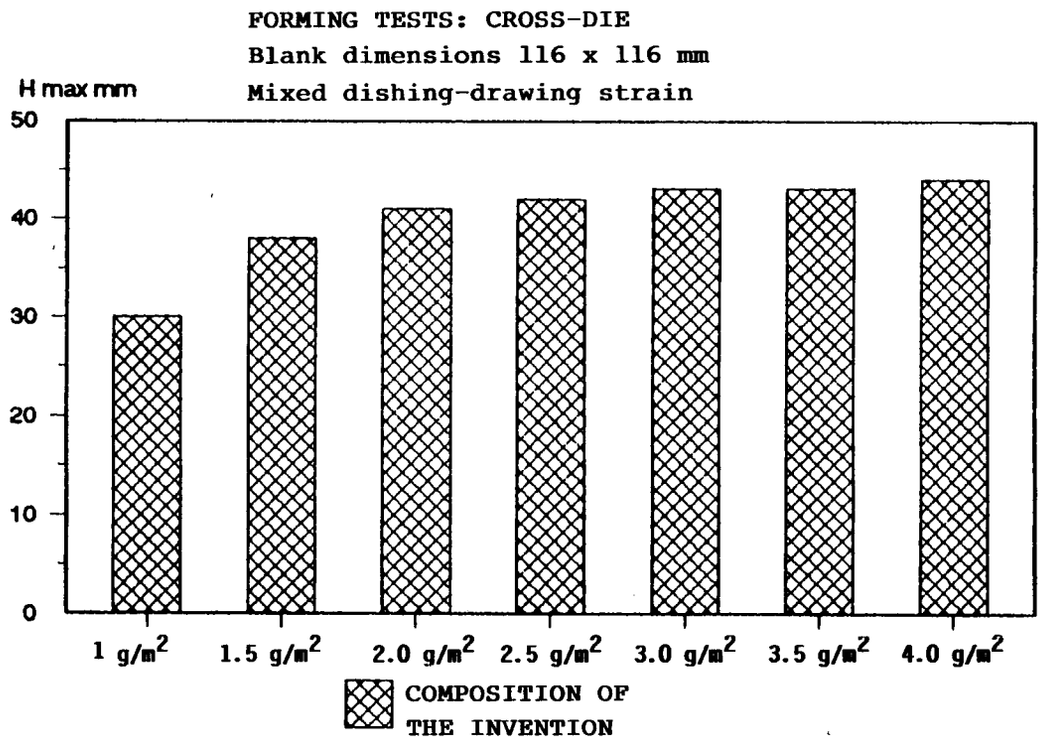
8. A forming oil composition according to claim 1, characterized in that it comprises:
a) 5-10% polyethoxylated dodecanoamine, containing 5 ethoxide groups;
b) 1-2% ethanol;
c) 3-5% of a solution containing 35% acrylic resin, 8.4% ammonia, 3% isopropanol, 1.5% propylene glycol, and 52.1% water;
d) 1-3% of a mixture of fatty acids amine salts and butylammonium caprilate;
e) an amount of a 70:30 water/2-ethyl-1,3-hexanediole medium sufficient to 100 parts (volume).

FIG. 1

B



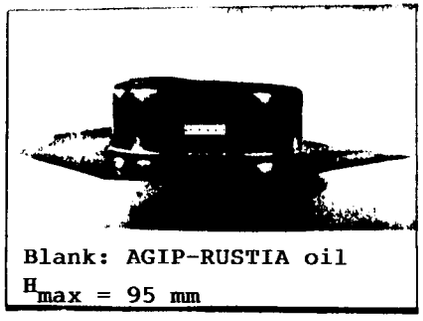
A



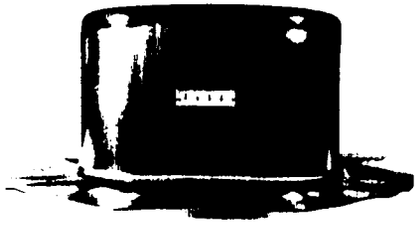
FORMING DEPTH AS A FUNCTION OF THE FORMING OIL THICKNESS

FIG. 2

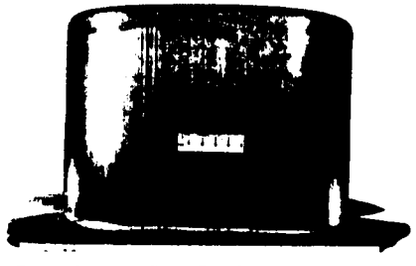
B



Blank: AGIP-RUSTIA oil
H_{max} = 95 mm



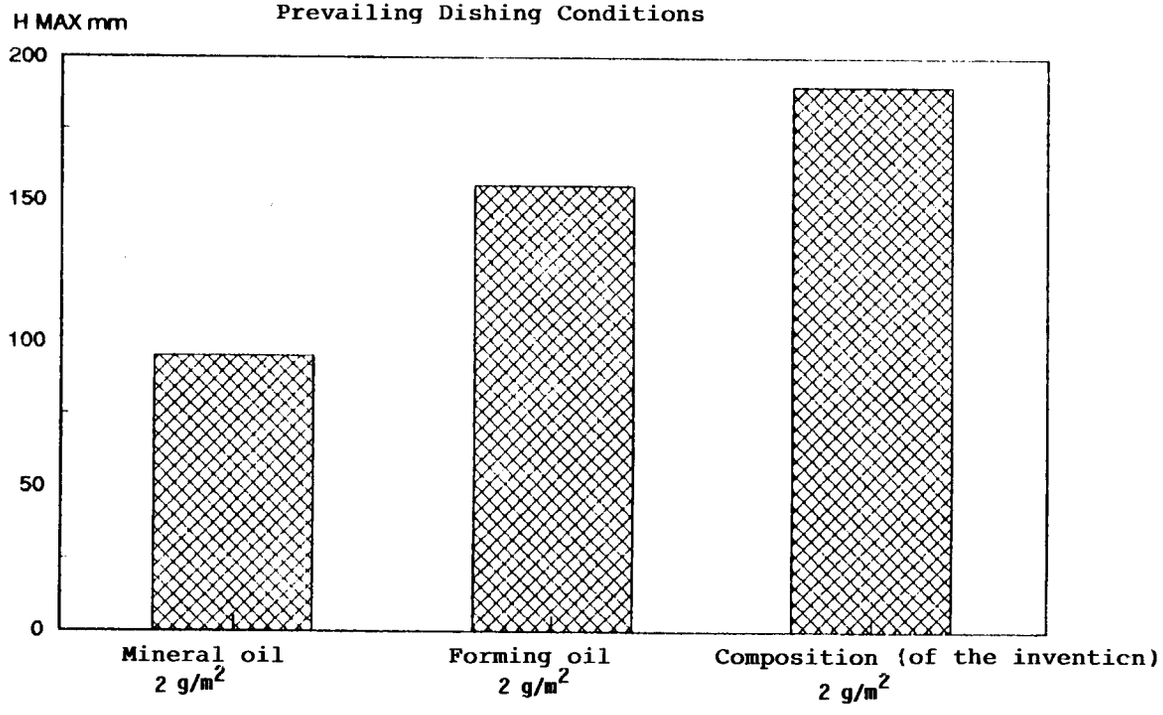
Blank: IMBUTEX oil
H_{max} = 155 mm



Blank: oil of the composition
H_{max} => 180 mm

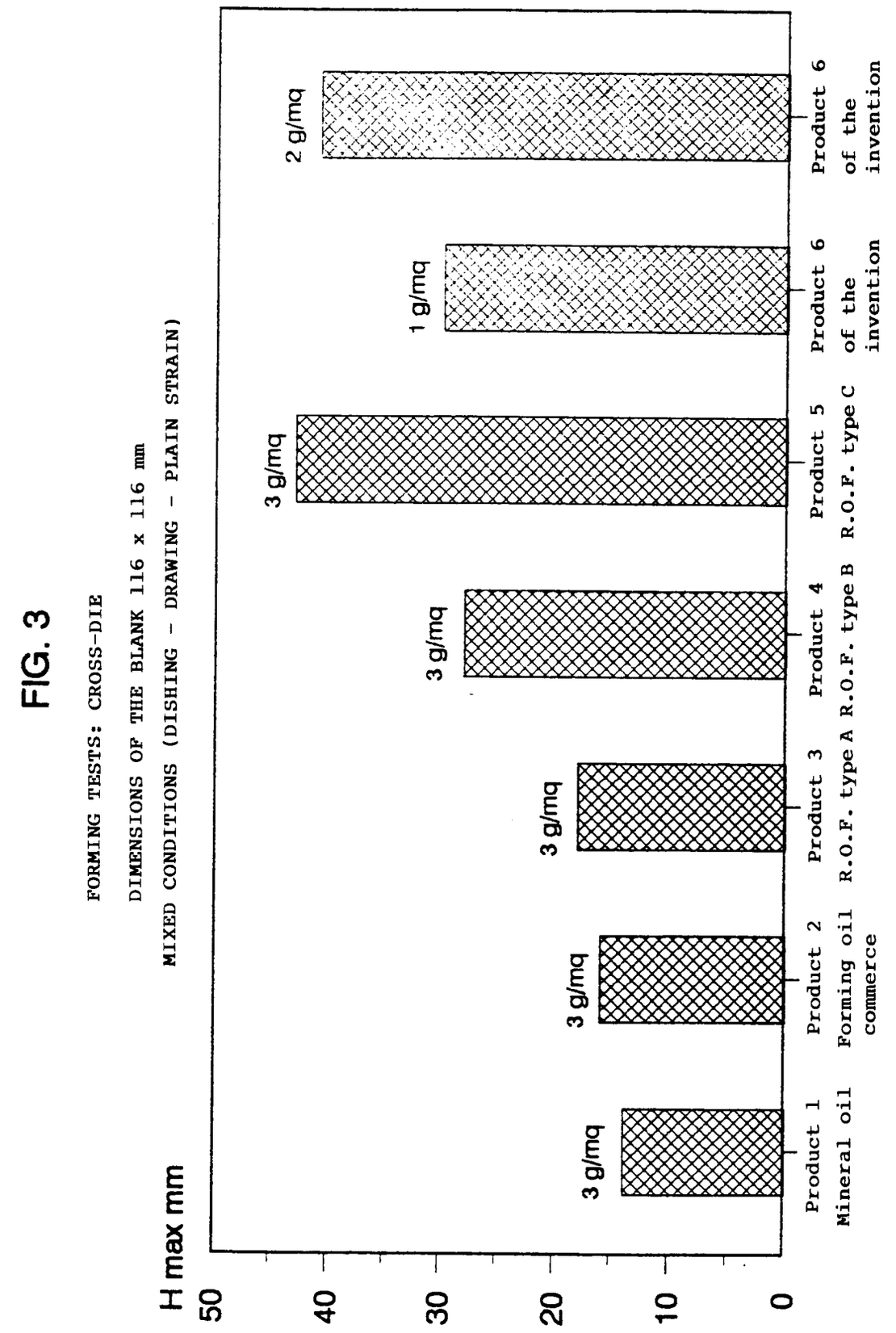
A

FORMING TEST: VESSELS (200 TON PRESS)
Blank Dimensions
Octagnon obtained from a 560 mm square
Prevailing Dishing Conditions



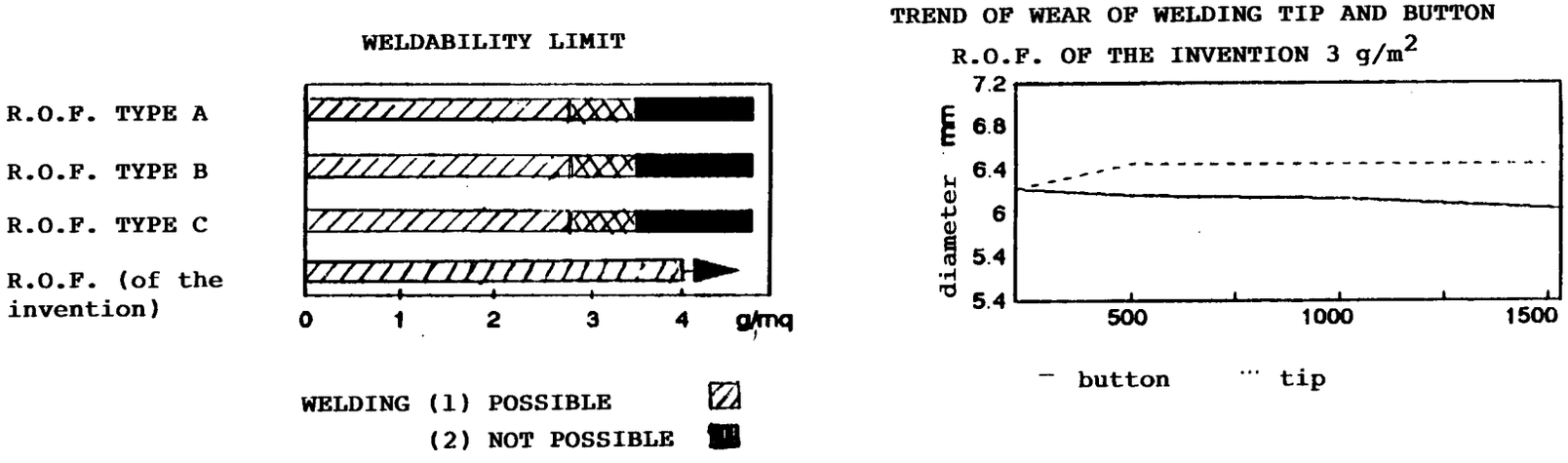
LUBRICATING POWER OF THE COMPOSITION OF THE INVENTION OVER MINERAL OILS

FIG. 3



LUBRICATING POWER OF THE INVENTIVE COMPOSITION OVER OTHER COMMERCIAL R.O.F. COMPOSITIONS

FIG. 4 ELECTRIC SPOT WELDABILITY



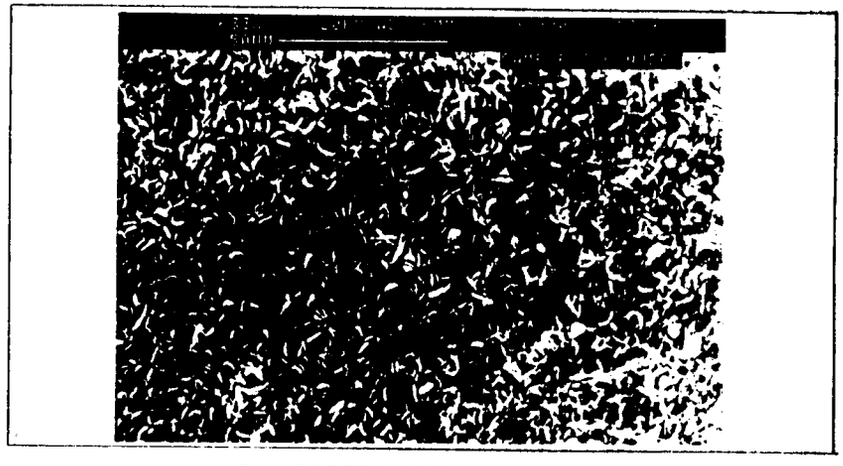
TEST CONDITIONS

ELECTRO-GALVANIZED STEEL 8+8 /u THICKNESS 0.80 mm
FRUSTOCONICAL ELECTRODES:Cu-Cr TYPE 328
CLAMPING FORCE 230 kg
NUMBER OF CYCLES: 12-15
CURRENT VALUE: 10-11 kA

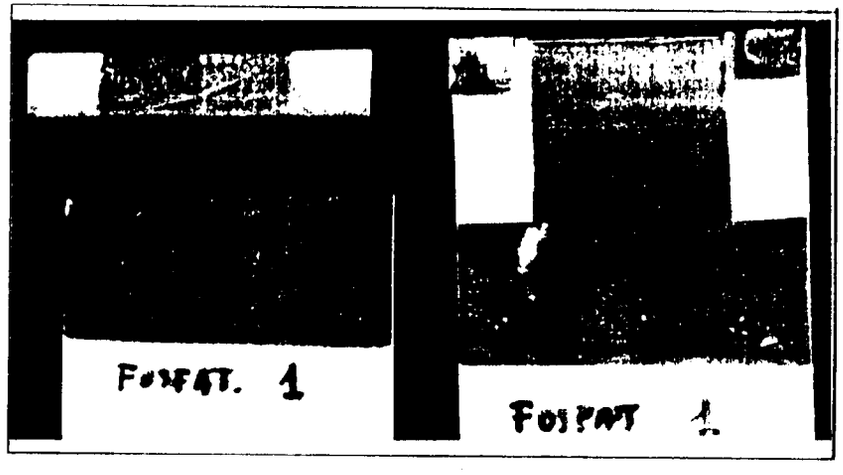
FIG. 5 REMOVABILITY AND PHOSPHATABILITY

DEGREASING AND PHOSPHATING - WORKING CYCLE:
AUTOMOTIVE INDUSTRY

DEGREASING	CLENSTONE 138 T = 50°C X 5'
RINSING	X 1'
ACTIVATION	7213 T. S. X 1'
PHOSPHATING	FOSTONE 33 T = 45°C X 3'
PASSIVATION	AQU. PASSIVATING AGENT X 1'
DRYING	T = 120°C



PHOSPHATED AREA (INTERSPACE)



SUPERIMPOSED SHEET STEEL PLATES, DISASSEMBLED
AFTER PHOSPHATING

EP 0 591 771 A1

FIG. 6

COMPARISON OF THE PROPERTIES OF THE FORMULATIONS

Formulation according to EXAMPLE	Lubricity Degree	Degree of Protection unprotected steel	Degree of Protection precoated with Zn and Zn alloys	Degree of Protection precoated with Al and Al alloys	Degree of Removability
1	3	5	4	3	5
2	5	4	4	4	5
3	5	5	4	4	5
4	4	3	5	4	5
5	4	4	5	4	4
6	5	3	4	4	5

RATING SCALE (1 worst, 5 best)

EP 0 591 771 A1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 5339

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X A	US-A-4 647 309 (R.E. HAYNER) * column 4, line 8 - line 11 * * column 4, line 34 * * column 4, line 55 - column 5, line 15 * * column 6, line 44 - line 47 * ---	1 2	C10M173/02 //C10N40/24
Y A	FR-A-2 160 405 (TRU-CHEMIE) * page 4; example 1 * * page 5; example 4 * ---	1 2	
Y	EP-A-0 438 801 (NIPPON OIL AND FATS COMPANY) * page 3, line 25 - line 31 * * page 3, line 44 - line 50 * * page 7, line 22 - line 26 * * page 7, line 38 - line 41 * ---	1	
A	EP-A-0 340 498 (LUBRITALIA) * page 3, line 23 - line 29 * * page 5, line 24 - line 31 * * page 7, line 34 - line 40 * * page 8, line 44 - line 47 * * page 9, line 47 - line 52 * ---	1,2,4,5	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C10M
A	WO-A-92 07924 (N. SMITH) * page 4, line 8 - line 13 * * page 4, line 22 - line 28 * * page 5, line 22 - line 30 * * page 7, line 24 - line 25 * ---	1,2,8	
A	US-A-4 846 986 (R.L.TRIVETT) * column 3, line 34 - line 42 * * column 4, line 25 * ---	1	
A	FR-A-2 105 236 (MOLLCO PATENTVERWERTUNGS AG) * claims 1,14,19,21 * -----	1,2,7	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 January 1994	Hilgenga, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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