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(54) **Lubricating oil for plastic working and articles worked by using the same.**

(57) A lubricating oil for plastic working contains a powder of a compound having a urea bond incorporated therein. The lubricating oil forms a thick lubricating coating having excellent thermal resistance and loading resistance on the frictional surface during working by simply applying it on the surface of a material or a mold and, therefore, effectively prevents occurrence of seizing, even in the production of moldings having a high degree of working or complex shapes. The plastic worked product has a coating of the lubricating oil on its surface which provides an excellent anticorrosive effect for steel stocks.

The oil may also contain at least one extreme-pressure additive selected from:

- (1) condensed phosphoric acid,
- (2) phosphite and phosphate esters,
- (3) organic sulfur compounds, and
- (4) organic chlorine compounds.

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TITLE OF THE INVENTION

LUBRICATING OIL FOR PLASTIC WORKING AND ARTICLES  
WORKED BY USING THE SAME

5 BACKGROUND OF THE INVENTION

This invention relates to lubricating oils for plastic working used in manufacturing machine parts by a method which comprises placing a steel stock or the like in a mold and pressing it with a hydraulic press, a  
10 machinery press or the like. More particularly, the present invention is concerned with lubricating oils for plastic working suitable particularly for use in backward extrusion working and composite extrusion working which cause a large area of a surface to be newly produced,  
15 leading to an increase in the surface area, and articles worked by using said oils.

As opposed to lubricating oils for bearings, lubricating oils for plastic working should exhibit lubricating capacities sufficient to withstand temperature  
20 rise attributable to heat generation accompanying deformation, friction, etc. during working, a pressure applied on a frictional surface and an increase in the area of a newly produced surface. In other words, mold life is directly influenced by lubricating capacities of  
25 a lubricating oil used.

The use of a lubricating oil which is not satisfactory in lubricating capacities brings a material

into direct contact with a mold, leading to seizing. If the seizing takes place over a large area, working pressure is increased to cause a local damage to or crack of the mold, which leads to not only a remarkable shortening in mold life but also occurrence of defective moldings and further makes it impossible to conduct working.

Conventional lubricating oils for cold working of steel stocks include a mineral<sup>oil</sup> or a synthetic oil, a mixture thereof (hereinafter referred to as "base oil") or a water-mixed base oil obtained by adding water to a base oil, each incorporating therein, for example, an oleaginous matter such as fatty acid or tallow, sulfur, phosphorus, chlorine-based extreme-pressure additive, an organometal-based extreme-pressure additive such as zinc dithiophosphate (Zn-DTP) or a solid lubricant such as graphite or molybdenum disulfide as described in "SEKIYU SEIHIN TENKAZAI (additives for oil products)" (edited by Toshio Sakurai, published on May 15, 1973 by Saiwai Shobo, Japan). These lubricating oils for plastic working can be used for deep draw working and roll working which are low in both degree of working and deformation of the material. However, the use of the lubricating oils in working which is high in degree of working and brings about a high temperature and high pressure on the worked surface, or working for complex shapes causes seizing, because they are insufficient in capacity for forming a

lubricating coating having a satisfactory thermal resistance and loading resistance as well as for forming a lubricating coating on a newly produced surface.

Conventional methods of lubrication for working which is high in degree of working include a method in which a lubricant prepared by dispersing a solid lubricant in a solution obtained by diluting or dissolving a synthetic resin in a solvent is applied on the surface of a material to form a lubricating coating and a method which comprises  
10   subjecting the surface of a material for plastic working to phosphate coating treatment, treating the surface of the resulting coating with a treating solution composed mainly of sodium stearate for forming a metal soap coating and subjecting the material to plastic working.  
15   There is also known a method of lubrication in which the surface of the material is subjected to oxalate coating treatment in place of the phosphate coating treatment and the surface of the resulting coating is further subjected to metal soap coating treatment. These chemical coating  
20   treatments are excellent in prevention of seizing as compared with the lubrication by means of the above-mentioned lubricating oils for plastic working.  
Therefore, in general, the chemical coating treatment is practically used for lubrication in cold working for steel  
25   stocks. However, the chemical coating treatment method in which a lubricating coating is formed on a material by synthetic resin coating or a combination of phosphate

coating or oxalate coating treatment with metal soap coating treatment require a sufficient pretreatment and a strict process control. For example, when metal soap coating treatment is conducted after phosphate coating treatment, a material such as steel stock is degreased before immersed in a phosphate bath having a predetermined phosphate concentration to form a coating. Thereafter, the material is washed with water, neutralized, immersed in a metal soap bath having a predetermined metal soap concentration and then dried. In other words, the above method requires complicated steps. Further, when the treating solutions are deteriorated, there arises difficulties related to disposal of the resulting wastes. As is apparent from the foregoing, the above-mentioned prior-art methods have some advantages but involve problems more or less.

Lubricating oils for plastic working are extremely advantageous in that their use contributes to simplification of processing steps, because lubrication can be conducted by simply applying it to a material or a mold according to the customary method such as spraying or dropping. However, conventional lubricating oils for plastic working have not been used for a high degree of working which is conducted under severe working conditions, because they are unsatisfactory in formation of a lubricating coating and, therefore, tend to cause seizing.

In order to hold a large amount of a lubricant on the frictional surface for eliminating the above-mentioned drawbacks of the lubricating oils, there has been proposed the use of highly viscous liquid lubricants or greases having an excellent heat resistance, e.g., greases as described in U.S. Patent Nos. 4,065,395, 4,100,081 and 4,113,640, i.e., greases containing, as a thickener, a diurea or a polyurea obtained by reacting a monoamine or a diamine with an isocyanate in a base oil. When such greases are used for cold forging involving a high degree of working, a seizing preventing ability thereof is slightly improved to those of liquid lubricants but is considerably inferior to that of lubrication by the chemical coating treatment method.

The above-mentioned prior-art methods have some advantages but involve problems. Specifically, with respect to liquid lubricants, there arose a problem related to seizing resistance under such working conditions to produce a large amount of heat due to deformation as well as a large area of a new surface and to apply a high pressure on the surface. On the other hand, the chemical coating treatment method had drawbacks that it involved complicated treating steps and required much labor and cost because of occurrence of a number of accompanying operations such as waste water disposal.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a lubricating oil for plastic working which does not require any chemical coating treatment, but requires simply to be  
5 fed to the surface of a material or a mold according to the customary method by making use of an advantage of lubricating oils and exhibits a seizing resistance which may be comparable to that of the lubrication by the chemical coating treatment.

10 Conventional lubricating oils of this kind comprise a mineral oil or a synthetic oil as a base oil and, incorporated therein, an extreme-pressure additive comprising a sulfur-, chlorine- or phosphorus-containing organic compound and a solid lubricant such as graphite  
15 or molybdenum disulfide. However, such lubricating oils cannot be used for a high degree of working and complicated working, because mere application of such lubricating oils on a material etc. gives only a thin oil coating which easily leads to seizing as compared with  
20 chemical coating and synthetic resin coating. The present invention has at least partly eliminated such drawbacks.

The present inventors have made extensive and intensive studies to attain the above-mentioned object. As a result, the present inventors have found that a  
25 liquid lubricating oil comprising a base oil and a compound having a urea bond (hereinafter referred to as "urea lubricant") incorporated therein exhibits a

remarkably improved resistance to seizing and makes it possible to obtain highly worked moldings and moldings having complex shapes by means of cold forging by merely applying it on the surface of a metal stock or a mold.

5           According to the present invention, there is provided a lubricating oil for plastic working comprising a lubricating oil (hereinafter referred to as "base oil") and, incorporated therein, a component A comprising a compound having a urea bond and optionally a component B comprising  
10   at least one member selected from the group consisting of organic compounds containing phosphorus, sulfur or chlorine (hereinafter referred to as "phosphorus-, sulfur- or chlorine-based extreme-pressure additive") and condensed phosphoric acid. The invention also provides a plastic working method using such a lubricating oil.

15           The lubricating oil for plastic working according to the present invention forms a thick lubricating coating having excellent thermal resistance, lubricity and loading resistance between a material and a mold by simply applying it on the surface of a material or a mold by a  
20   customary method such as spraying, brushing or dropping and, therefore, exhibits a remarkably improved resistance to seizing even in manufacture of plastic working products having a high degree of working or complex shapes.

          The urea lubricants, i.e., components A in the  
25   present invention include diurea, tetraurea and polyurea. These urea lubricants can easily be produced by reacting an amine with an isocyanate, which are starting materials,

in an inert organic solvent, e.g., toluene. Examples of monoamines which may be used in the reaction include pentylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, dodecylamine, hexadecylamine, octadecylamine, octadecylamine, octadecylamine, abietylamine, aniline, toluidine, naphthylamine, cumylamine, bornylamine, butylamine, benzylamine, phenethylamine, laurylamine, palmitylamine, methylamine, isoamylamine, cyclohexylamine, and 2-methyl-6-ethylaniline. Examples of diamines which may be used in the reaction include ethylenediamine, propanediamine, butanediamine, hexanediamine, dodecanediamine, octanediamine, hexadecanediamine, cyclohexanediamine, cyclooctanediamine, phenylenediamine, tolylenediamine, xylylenediamine, dianilinomethane, ditoluidinomethane, bisaniline, bistoluidine, diaminoheptane, diaminononane, diaminodecane, diaminopentane, benzidine, diaminodiphenylmethane and methylenebis(2-chloroaniline).

Examples of triamines which may be used in the reaction include diethylenetriamine, dipropylenetriamine and N-methyldiethylenetriamine. Examples of other polyamines which may be used in the reaction include triethylenetriamine, tetraethylenepentaamine and pentaethylenehexaamine. Examples of monoisocyanates which may be used in the reaction include hexyl isocyanate, decyl isocyanate, dodecyl isocyanate, tetradecyl

isocyanate, hexadecyl isocyanate, phenyl isocyanate, cyclohexyl isocyanate, tolyl isocyanate, xylylisocyanate, cumenyl isocyanate, cyclooctyl isocyanate, butyl isocyanate, methyl isocyanate, ethyl isocyanate, isopropyl isocyanate, chloroethyl isocyanate, chlorophenyl isocyanate, dichlorophenyl isocyanate, naphthyl isocyanate, octadecyl isocyanate, phenyl isocyanate and tolylisocyanate. Examples of diisocyanates which may be used in the reaction include xylylene diisocyanate, hexylene diisocyanate, decylene diisocyanate, octadecylene diisocyanate, phenylene diisocyanate, tolidine diisocyanate, tolylene diisocyanate, methylenebisphenylene isocyanate, naphthylene diisocyanate and polymethylenepolyphenyl isocyanate.

The reaction product obtained by reacting the above-mentioned raw materials in an organic solvent is filtered, dried and pulverized to obtain a urea lubricant powder. The particle diameter of the powder may arbitrarily be selected taking into consideration working conditions, dispersion stability of the powder, etc., and is generally in the range of 0.5 to 500 $\mu$ m. In the case of backward extrusion working, composite extrusion working or manufacture of articles having complex shapes or a high degree of working which produces a large area of a new surface, a preferred particle diameter is in the range of 35 to 500 $\mu$ m.

When a further improvement in lubricity of the urea lubricant is required, a powder comprising a urea lubricant powder of which the surface is coated with, e.g., a synthetic wax may also be used.

5        Examples of phosphorus-based extreme-pressure additive which is one of the component B include phosphites, e.g., tertiary phosphites such as triphenyl phosphite, tris(nonylphenyl) phosphite, triisooctyl phosphite, diphenyl isodecyl phosphite, phenyl diisodecyl  
10       phosphite, tristearyl phosphite, trioleyl phosphite and trilauryl trithiophosphite and secondary phosphites such as di-2-ethylhexyl hydrogen phosphite, dilauryl hydrogen phosphite and dioleyl hydrogen phosphite and phosphates  
15       such as trimethyl phosphate, tributyl phosphate, triphenyl phosphate, tricresyl phosphate, octyl diphenyl phosphate, trilauryl phosphate, tristearyl phosphate, trioleyl  
20       phosphate, monobutyl phosphate, dibutyl phosphate, monoisodecyl phosphate, trichloroethyl phosphate, methyl acid phosphate, isopropyl acid phosphate, butyl acid  
25       phosphate, 2-ethylhexyl acid phosphate, lauryl acid phosphate, stearyl acid phosphate and oleyl acid phosphate. Examples of sulfur-based extreme-pressure  
additive which is one of the component B include sulfurized fat and oil, dibenzyl sulfide disulfide, polysulfide, di-tert-butyl sulfide, di-n-butyl disulfide and  
polyoxyethylene polysulfide. Examples of chlorine-based extreme-pressure additive which is one of the component B

incude chlorinated paraffin, chlorinated fat and oil and pentachlorinated fatty acid. Examples of condensed phosphoric acid which is one of the component B include pyrophosphoric acid and polyphosphoric acid.

5           Examples of the base oil to which the components A and B are added include mineral oil, dibasic acid diester oil, neopentyl polyol ester oil,  $\alpha$ -olefin oil, fluoro ester, silicate ester oil, polyglycol oil, silicone oil, polyphenyl ether oil and polybutene oil. The properties  
10 of the above-mntioned base oils may properly be determined taking into consideration working conditions and operating conditions. In general, a preferred viscosity of the base oil is in the range of about 10 to 500 cSt at 40°C.

          Although the amount of the urea lubricant powder or  
15 coated urea lubricant powder to be incorporated should properly be determined taking into consideration the degree of working of the intended molded parts and working conditions, said amount is 1 to 25 wt% in the case of ordinary extrusion working. However, a preferred amount  
20 of incorporation in the case of backward extrusion working and composite extrusion working which bring about a large area of a new born surface (nascent surface) and, therefore, brings about an increase in the surface area is 1.5 to 25 wt%. Therefore, the amount of the component  
25 A to be incorporated in the base oil may properly be determined taking into consideration the kind of material, degree of working, shapes of intended worked articles,

method of feeding the lubricating oil, etc. However, a preferred amount of the component A is generally in the range of 1.5 to 25 wt%.

When the amount of the component A is below the  
5 above-mentioned range, the effect attained by its addition is small, leading to seizing. On the other hand, even if the component is excessively added, the effect exceeding a certain limit cannot be attained. Therefore, it is preferred that the component A be used in an amount in  
10 the above-mentioned range.

The urea lubricant which is incorporated in the base oil is in powdery form, and the diameter of the powder particles should properly be determined taking into consideration the degree of working, method of working,  
15 dispersion stability, etc. In the case of ordinary extrusion working, a powder having a particle diameter of 0.5 to 500 $\mu$ m is used. However, a preferred particle diameter of the powder used in backward extrusion working and composite extrusion working which bring about a large  
20 area of a new born surface and, therefore, brings about an increase in the surface area is 35 to 500 $\mu$ m. In general, it is preferred that the larger the increase in the surface area of the moldings, the larger the particle diameter of the powder to be incorporated.

25 The urea lubricant or coated urea lubricant is used in the form of a dispersion in the above-mentioned base oil. Although the dispersant used varies depending on

the kinds of base oil and urea lubricating oil, examples of such dispersants are polymethacrylate, ethylene-olefin copolymer and polyisobutylene. Another method for attaining effective dispersion is to adjust the specific gravity of the base oil to that of the urea lubricant.

The lubricating oil for plastic working of the present invention may contain known organic extreme-pressure additives containing chlorine, phosphorus or sulfur, antioxidants and anticorrosive agents.

The lubricating oil for plastic working of the present invention is used by applying it on the surface of a material for plastic working or a mold by known methods such as spraying, dropping, immersion, roll coating, etc.

The article produced by plastic working according to the present invention has a coating on its surface and, therefore, has anticorrosive properties. The powder of the compound having a urea bond forms a coating on the worked article together with the lubricating oil after working.

Prior to the description on the function of the components of the lubricating oil for plastic working of the present invention, some description will be given on a lubrication mechanism of liquid lubricants in deep draw working, roll working, etc. With respect to the lubrication mechanism, reference may be made to Mitsugu Tokizawa, Lubrication in the Plastic Working of Metals

("JUNKATSU", Vol. 18, No. 3, (1973) pp. 193 - 201) and  
Yasuo Kasuga, Lubrication Mechanism in Plastic Working  
("SOSEI TO KAKO", Vol. 9, No. 87, (1968) pp. 202 - 214).

As is described in the above references, a liquid

5 lubricant which has been brought into the space between  
the face of a material and a face of a mold is confined in  
the recessed portions present in the surface of the  
material during working. With the proceeding of plastic  
deformation, the protruded portions on the surface are  
10 pressed down to cause the liquid lubricant remaining in  
the recessed portions to be forcibly discharged therefrom,  
which causes the discharged lubricant to be fed to the  
flat face formed by pressing to form a thin oil coating.  
When the liquid lubricant contains a phosphorus-,  
15 chlorine- or sulfur-based extreme-pressure additive, an  
extreme-pressure coating is formed on the surface of the  
material due to the heat generated accompanying plastic  
deformation, which contributes to prevention of seizing.  
Although lubrication is conducted based on the above-  
20 mentioned mechanism also in the case of working which is  
high in degree of working and large in an increase in the  
surface area, the formation of an extreme-pressure coating  
is insufficient at the frictional surfaces exposed to  
high temperature and high pressure, which leads to  
25 occurrence of seizing.

The lubrication mechanism of a liquid lubricant for  
plastic working containing a urea lubricant powder

dispersed therein according to the present invention is the same as that described above. However, in the case of the liquid lubricant of the present invention, the powdery urea lubricant is confined together with the base oil in the recessed portions present on the surface of the material. Since the protruded portions present on the surface of the material is pressed down at a high temperature under a high pressure, the powdery urea lubricant is allowed to dissolve to form a highly viscous oil or rolled and fed to the frictional surfaces in the form of a mixture with the base oil, with the proceeding of deformation of the material. A thick lubricating coating is formed on the frictional surface to prevent direct contact of the material with a mold. A coated urea lubricant for improving the lubricity of the urea lubricant functions in the same manner as mentioned above.

When the urea lubricant and coated urea lubricant are incorporated in an amount below the above-mentioned range or small in particle diameter, any satisfactory lubricating coating cannot be formed. On the other hand, the incorporation thereof in excessive amounts leads to an increase in the viscosity, which not only causes lowering in applicability on the surface of a metal stock and a mold, but also gives no further improved effect. Therefore, it is preferred that the amounts of the urea lubricating oil and coated urea lubricating oil incorporated be in the above-mentioned range.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the relationship between the particle diameter of a diurea powder and the maximum allowable working temperature in a forward extrusion working;

FIG. 2 is a graph showing the relationship between the particle diameter of a diurea powder and the maximum allowable working temperature in a backward extrusion working;

FIG. 3 is a graph showing the amount of a diurea powder incorporated and the maximum allowable working temperature in a forward extrusion working and a backward extrusion working;

FIG. 4 is an illustrative view of a forward extrusion working method, in which FIG. 4(a) is a cross-sectional view illustrating a state in which a workpiece coated with a liquid lubricant has been inserted into a mold and FIG. 4(b) is a cross-sectional view illustrating a state in which a punch has been pressed down to extrude the workpiece from the mold;

FIG. 5 is an illustrative view of a backward extrusion working method, in which FIG. 5(a) is a cross-sectional view illustrating a state in which a workpiece coated with a liquid lubricant has been inserted into a mold and FIG. 5(b) is a cross-sectional view illustrating a state in which a punch has been pressed down for working of the workpiece;

Fig. 6 is a longitudinal sectional view of a workpiece used for forging;

FIG. 7 is a longitudinal sectional view of a cylinder for a video tape recorder produced by forging;

5        FIG. 8 is a longitudinal sectional view of a photosensitive drum for electrophotography produced by forging; and

FIG. 9 is a longitudinal sectional view of a pinion for automobiles produced by forging.

10

#### EXAMPLES

The examples of the present invention will now be described together with comparative examples. The present  
15        invention should not be construed to be limited to these examples.

First, some description will be given with respect to criteria for evaluating working performance.

Working performance of liquid lubricants was  
20        evaluated by the forward extrusion working method as shown in FIG. 4 and the backward extrusion working method as shown in FIG. 5. Specifically, a mold 3 was equipped with a band heater 4. The temperature of the mold 3 was stepwise raised by 5 to 10°C a time. At each temperature,  
25        a material 2 coated with a liquid lubricant was inserted into the mold 3, and 10 to 15 pieces of the material were worked at the same temperature at a press-down rate of a

punch 1 of 8 mm/s to determine a mold temperature at which the material could be worked without causing any seizing (maximum allowable working temperature). The higher the maximum allowable working temperature, the more excellent the thermal resistance and loading resistance of the lubricating coating.

# 1. Working Conditions:

## 1.1 Forward Extrusion Working Method

### (a) Material and Dimensions

| material | outside dia.<br>(mm) | length<br>(mm) | surface roughness<br>( $\mu$ m) |
|----------|----------------------|----------------|---------------------------------|
| SCM415   | 9.9                  | 30             | Ra 1.5                          |

### (b) Principal Dimensions of Mold

| material                     | land inside<br>dia.<br>(mm) | extrusion<br>angle<br>( $^{\circ}$ ) | drawing<br>dia.<br>(mm) | degree of<br>working<br>(%) |
|------------------------------|-----------------------------|--------------------------------------|-------------------------|-----------------------------|
| hard<br>metal V <sub>5</sub> | 10                          | 120                                  | 5                       | 75                          |

## 1.2 Backward Extrusion Working

### (a) Material and Dimensions

| material | outside dia.<br>(mm) | length<br>(mm) | surface roughness<br>( $\mu$ m) |
|----------|----------------------|----------------|---------------------------------|
| SCM415   | 20                   | 30             | Ra 2.0                          |

### (b) Principal Dimensions of Mold

| material                     | land inside<br>dia.<br>(mm) | punch<br>dia.<br>(mm) | depth of<br>boring<br>(mm) | degree of<br>working<br>(%) |
|------------------------------|-----------------------------|-----------------------|----------------------------|-----------------------------|
| hard<br>metal V <sub>5</sub> | 20.1                        | 16.1                  | 48                         | 64                          |

EXAMPLE 1

60 g (0.283 mol) of o-tolidine was added to 600 ml of dried toluene, and the mixture was heated at 110 to 115°C to dissolve the o-tolidine in the toluene. To the  
5 resulting solution was dropwise added 67.3 g (0.565 mol) of phenyl isocyanate at 106°C over 15 min. The mixture was stirred at 110 to 113°C for 4 hr, allowed to cool at room temperature, filtered and dried to obtain 117.8 g of a white crystalline diurea [4,4'-(3,3'-  
10 dimethyldiphenylene)-diphenylurea]. The diurea thus obtained was pulverized and classified to obtain a diurea powder having a particle diameter of 63 to 88 $\mu$ m. 10% by weight of the diurea powder was incorporated in a mineral oil (viscosity at 40°C: 150 mm<sup>2</sup>/s) at ordinary  
15 temperature, and the mixture was stirred at 130 rpm for 10 min to obtain a liquid lubricant of the present invention comprising a diurea powder dispersed in the oil. The results of evaluation on working performance of the liquid lubricant thus obtained are shown in Table 1.  
20 The compositions of the comparative lubricants are shown below.

COMPARATIVE EXAMPLE 1 (commercially available processing oil)

25 base oil: mineral oil the remainder (amount)  
extreme-pressure additive: a fatty acid content of 43 wt%, a chlorine content of 12 wt%, and a sulfur content of 6 wt%.

COMPARATIVE EXAMPLE 2 (urea grease obtained by reacting amine with isocyanate in a base oil)

base oil: mineral oil (88 wt%)

thickner: diurea (10 wt%)

5 additive: antioxidant (2 wt%)

The above grease is in the form of semi-solid to solid obtained by agglomeration of the finely divided powder thickener in a colloidal form.

10 EXAMPLE 2

90.8 g (0.84 mol) of p-phenylenediamine was added to 1400 ml of dried toluene. To the resulting mixture was dropwise added 200 g (1.68 mol) of phenyl isocyanate at 100 to 110°C over 1 hr. The mixture was stirred at 110 to 112°C for 4 hr, allowed to cool at room temperature, filtered and dried to obtain 283.8 g of a white crystalline diurea [p-phenylenediphenylurea]. The diurea thus obtained was pulverized and classified to obtain a diurea powder having a particle diameter of 63 to 88 m. 10% by weight of the diurea powder was incorporated in a mineral oil (viscosity at 40°C: 150 mm<sup>2</sup>/s (cSt)) at ordinary temperature, and the mixture was stirred at 130 rpm for 10 min to obtain a liquid lubricant of the present invention comprising a diurea powder dispersed in the oil. The results of evaluation on working performance of the liquid lubricant thus obtained are shown in Table 1.

## EXAMPLE 3

13.9 g (0.080 mol) of tolylene diisocyanate was dissolved in dried toluene at 25 to 33°C. To the resulting solution was dropwise added 20.5 g (0.16 mol) of p-chloroaniline. The mixture was stirred at 110°C for 5 hr, allowed to cool at room temperature, filtered and dried to obtain 33.6 g of a white crystalline diurea [1-methyl-2,4-bis(4-chlorophenylureido)benzene]. The diurea thus obtained was pulverized and classified to obtain a diurea powder having a particle diameter of 63 to 88  $\mu$ m. 10% by weight of the urea powder was incorporated in a mineral oil (viscosity at 40°C: 150 mm<sup>2</sup>/s) at ordinary temperature, and the mixture was stirred at 300 rpm for 10 min to obtain a liquid lubricant of the present invention comprising a diurea powder dispersed in the oil. The results of evaluation on working performance of the liquid lubricant thus obtained are shown in Table 1.

## EXAMPLE 4

17.4 g (0.1 mol) of tolylene diisocyanate was dissolved in 180 ml of dried toluene. To the resulting solution was dropwise added 18.6 g (0.20 mol) of aniline at 27 to 34°C while stirring. The mixture was stirred at 75 to 80°C for 5 hr, allowed to cool at room temperature, filtered and dried to obtain 35.5 g of a white crystalline diurea [1-methyl-2,4-diphenylureidobenzene]. The diurea thus obtained was pulverized and classified to obtain a

diurea powder having a particle diameter of 63 to 88 $\mu$ m.  
10% by weight of the urea powder was incorporated in a  
mineral oil (viscosity at 40°C: 150 mm<sup>2</sup>/s) at ordinary  
temperature, and the mixture was stirred at 130 rpm for  
5 10 min to obtain a liquid lubricant of the present  
invention comprising a diurea powder dispersed in the  
oil. The results of evaluation on working performance of  
the liquid lubricant thus obtained are shown in Table 1.

#### 10 EXAMPLE 5

3 g (0.05 mol) of ethylenediamine and 26 g (0.10  
mol) of oleylamine were added to 200 ml of dried toluene  
of 60 to 75°C. 50 ml of dried toluene containing 17.4 g  
(0.10 mol) of tolylene diisocyanate dissolved therein was  
15 dropwise added to the above-prepared amine solution while  
stirring over 1 hr. Subsequently, the mixture was heated  
at 110°C for 5 hr to obtain a print-like reaction product.  
The reaction product was vacuum dried to obtain 40.2 g of  
a light yellow crystalline polyurea [1,2-ethylenebis(2-  
20 methyl-5'-octadecylureidophenyl)urea]. The polyurea thus  
obtained was pulverized and classified to obtain a  
polyurea powder having a particle diameter of 63 to 88 $\mu$ m.  
10% by weight of the urea powder was incorporated in a  
mineral oil (viscosity at 40°C: 150 mm<sup>2</sup>/s) at ordinary  
25 temperature, and the mixture was stirred at 300 rpm for  
10 min to obtain a liquid lubricant of the present  
invention containing a polyurea powder dispersed therein.

The results of evaluation on working performance of the liquid lubricant thus obtained are shown in Table 1.

#### EXAMPLE 6

5           A mixture of 3.6 g (0.06 mol) of ethylenediamine with octadecylamine (0.10 mol) is heated at 60°C to form a solution. Separately, 17.4 g of a mixture of 2,4-tolylene diisocyanate with 2,6-tolylene diisocyanate in a ratio of 80 : 20 was added to dried toluene. The mixture  
10           was subjected to dispersion at about 30°C. The resulting dispersion was dropwise added to the above-prepared hot solution while stirring. The mixture was stirred at 80°C for 5 hr, allowed to cool at room temperature, filtered and dried to obtain 27.9 g of a white crystalline diurea.  
15           The diurea thus obtained was pulverized and classified to obtain a diurea powder having a particle diameter of 63 to 88 $\mu$ m. 10% by weight of the urea powder was incorporated in a mineral oil (viscosity at 40°C: 150 mm<sup>2</sup>/s) at ordinary temperature, and the mixture was  
20           stirred at 130 rpm for 10 min to obtain a liquid lubricant of the present invention containing a diurea dispersed therein. The results of evaluation on working performance of the liquid lubricant thus obtained are shown in Table 1.

25           As is apparent from Table 1, the liquid lubricants of the present invention are higher in the temperature of a mold at which seizing occurs than those of comparative

examples, i.e., are superior in working performance to the comparative lubricants.

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Table 1

| EX.            | isocyanate                                             | amine                             | amount of urea incorp. (wt%) | max. allowable working temp. (°C) |                                |
|----------------|--------------------------------------------------------|-----------------------------------|------------------------------|-----------------------------------|--------------------------------|
|                |                                                        |                                   |                              | forward extrusion working 1)      | backward extrusion working 2)  |
| 1              | phenyl isocyanate                                      | o-tolidine                        | 10                           | 150                               | 70                             |
| 2              | ditto                                                  | p-phenylenediamine                | 10                           | 150                               | 70                             |
| 3              | tolylene diisocyanate                                  | p-chloroaniline                   | 10                           | 120                               | 85                             |
| 4              | ditto                                                  | aniline                           | 10                           | 150                               | 80                             |
| 5              | ditto                                                  | ethylenediamine<br>oleylamine     | 10                           | 150                               | 70                             |
| 6              | 2,4-tolylene diisocyanate<br>2,6-tolylene diisocyanate | ethylenediamine<br>octadecylamine | 10                           | 150                               | 70                             |
| COMP.<br>EX. 1 | processing oil containing extreme pressure additive    |                                   |                              | 80                                | seizing occurred at room temp. |
| COMP.<br>EX. 2 | urea grease (diurea: 10 wt%)                           |                                   |                              | 30                                | 30                             |

1) degree of working: 75%

2) degree of working: 64%

## EXAMPLE 7

The diureas as obtained in EXAMPLES 1 and 3 are separately incorporated in an amount of 10% by weight to a mineral oil having a viscosity of 150 mm<sup>2</sup>/s (cSt) at 40°C. The relationship between the particle diameter of the powder and the maximum allowable working temperature was determined by the forward extrusion working method and the backward extrusion working method using the above-prepared samples. FIG. 1 shows the results with respect to a degree of working of 75% in the forward extrusion, while FIG. 2 shows the results with respect to a degree of working of 64% in the backward extrusion. As is apparent from Fig. 1, the maximum allowable working temperature increases rapidly when the particle diameter of the powder exceeds about 0.5μm. Further, as is apparent from FIG. 2, the maximum allowable working temperature increases rapidly when the particle diameter of the powder exceeds about 35μm.

## 20 EXAMPLE 8

The same diurea as obtained in EXAMPLE 3 was incorporated in an amount of 0.6 to 12 wt% to a mineral oil having a viscosity of 150 mm<sup>2</sup>/s (cSt) at 40°C. The relationship between the amount of the powder incorporated and the maximum allowable working temperature was determined by the forward extrusion working method and the backward extrusion working method. The results are

shown in FIG. 3, in that, curve 10 shows the relationship with respect to the forward extrusion working method, curve 20 the backward extrusion working method.

As is apparent from FIG. 3, the effect of addition is observed when the amount of incorporation is 1 wt% or larger in the forward extrusion working method and 1.5 wt% or larger in the backward extrusion working method.

#### EXAMPLE 9

The diurea and polyurea respectively obtained in EXAMPLES 4 and 5 and comprising particles of which the diameters were adjusted to 63 to 88 $\mu$ m were separately added in an amount of 10 wt% to the synthetic oil as indicated in Table 2 and dispersed therein under the same stirring conditions as in EXAMPLES 4 and 5 to obtain liquid lubricants. Evaluations on the maximum allowable working temperature of the above-prepared liquid lubricants were conducted by the forward extrusion working method and the backward extrusion working method.

As is apparent from Table 2, the liquid lubricants of the present invention containing a diurea or polyurea incorporated therein are higher in the maximum allowable working temperature than those obtained in COMPARATIVE EXAMPLES 1 and 2 as indicated in Table 1, i.e., are superior in working performance to the comparative lubricants.

Table 2

| EX. 9 | urea                             | synthetic oil                               | viscosity<br>at 40°C<br>mm <sup>2</sup> /s (cst) | max. allowable working temp. (°C) |                                  |
|-------|----------------------------------|---------------------------------------------|--------------------------------------------------|-----------------------------------|----------------------------------|
|       |                                  |                                             |                                                  | forward extrusion<br>working 1)   | backward extrusion<br>working 2) |
| EX. 9 | diurea<br>obtained<br>in EX. 4   | α-olefin oil                                | 100                                              | 150                               | 70                               |
|       |                                  | polyol ester oil                            | 56                                               | 140                               | 60                               |
|       |                                  | polybutene oil                              | 100                                              | 90                                | 40                               |
|       |                                  | polyphenyl ether oil                        | 230                                              | 100                               | 45                               |
|       |                                  | fluorosilicone oil                          | 200                                              | 155                               | 60                               |
|       | polyurea<br>obtained<br>in EX. 5 | mineral oil + polyol<br>ester oil (50 : 50) | 105                                              | 160                               | 70                               |
|       |                                  | α-olefin oil                                | 100                                              | 150                               | 75                               |
|       |                                  | polyol ester oil                            | 56                                               | 135                               | 60                               |
|       |                                  | polybutene oil                              | 100                                              | 100                               | 45                               |
|       |                                  | polyphenyl ether oil                        | 230                                              | 100                               | 60                               |
| EX. 9 | polyurea<br>obtained<br>in EX. 5 | fluorosilicone oil                          | 200                                              | 110                               | 70                               |
|       |                                  | mineral oil + polyol<br>ester oil (50 : 50) | 105                                              | 150                               | 70                               |

1) degree of working: 75%

2) degree of working: 64%

EXAMPLES 10 to 23

60 g of o-tolidine was added to 600 ml of dried toluene, and the mixture was heated at 110 to 115°C to dissolve the o-tolidine in the toluene. To the resulting solution was dropwise added 67.3 g of phenyl isocyanate at 106°C. The mixture was stirred at 110 to 113°C for about 4 hr, allowed to cool at room temperature, filtered and dried to obtain a white crystalline diurea. The diurea thus obtained was pulverized to obtain a urea lubricant having an average particle diameter of 90 $\mu$ m which is the component A. In a mineral oil as a base oil having a viscosity of 150 cSt at 40°C were incorporated the above-obtained component A and phosphorus-, sulfur-or chlorine-based extreme-pressure additives as the component B in amounts as indicated in Table 3 to obtain lubricating oils for plastic working of the present invention. The lubricating oils thus obtained were applied on the surface of a chromium-molybdenum steel (SCM415) material 2 having a diameter of 10 mm or 20.1 mm and a length of 30 mm by dropping. Thereafter, molds 3 (made of a hard metal, V<sub>5</sub>) for the forward extrusion working method as shown in FIG. 4 and for backward extrusion working method as shown in FIG. 5 were equipped with a band heater 4. The temperature of the molds 3 was stepwise raised by 5 to 10°C a time, and 10 pieces of the material 2 were worked with a punch 1 with the same condition for evaluating maximum allowable working temperature.

The forward extrusion working was conducted under the following conditions:

material: a diameter of 10 mm and a length of 30 mm  
extrusion angle: 120°  
5 drawing diameter: 5 mm  
degree of working (reduction of cross-sectional area):  
75%  
press-down rate of punch: 8 mm/s

10 The backward extrusion working was conducted under the following conditions:

material: a diameter of 20.1 mm and a length of 30 mm  
punch diameter: 16.1 mm  
degree of working: 64%  
depth of bore in worked article: 48 mm  
15 press-down rate of punch: 8 mm/s

The compositions of the processing oils which have conventionally been used are shown in Table 4. The maximum allowable working temperature on these processing oils were also determined under the above-mentioned  
20 conditions. The results are shown in Table 5. As can be seen from Table 5, the lubricating oils for plastic working of the present invention exhibit a high maximum allowable working temperature, i.e., exhibit an excellent resistance to seizing.

Table 3

| No. | base oil       |                               |                               | component A urea lubricant powder               |                      |                         |                               | component B extreme-pressure additive |                               |
|-----|----------------|-------------------------------|-------------------------------|-------------------------------------------------|----------------------|-------------------------|-------------------------------|---------------------------------------|-------------------------------|
|     | kind           | viscosity<br>at 40°C<br>(cSt) | amount of<br>incorp.<br>(wt%) | raw materials for pre-<br>paration of lubricant |                      | average<br>dia.<br>(μm) | amount of<br>incorp.<br>(wt%) | kind                                  | amount of<br>incorp.<br>(wt%) |
|     |                |                               |                               | amine                                           | isocyanate           |                         |                               |                                       |                               |
| 10  | mineral<br>oil | 150                           | 80                            | o-tolidine                                      | phenyl<br>isocyanate | 90                      | 10                            | monobutyl phosphate                   | 10                            |
| 11  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | tributyl phosphate                    | "                             |
| 12  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | triphenyl phosphite                   | "                             |
| 13  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | dioleyl hydrogen phosphite            | "                             |
| 14  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | methyl acid phosphate                 | "                             |
| 15  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | oleyl acid phosphate                  | "                             |
| 16  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | pyrophosphoric acid                   | "                             |
| 17  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | sulfurized fat and oil                | "                             |
| 18  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | chlorinated paraffin                  | "                             |
| 19  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | pyrophosphoric acid                   | 5                             |
|     |                |                               |                               |                                                 |                      |                         |                               | dioleyl hydrogen phosphate            | 5                             |
| 20  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | tributyl phosphate                    | 5                             |
|     |                |                               |                               |                                                 |                      |                         |                               | sulfurized fat and oil                | 5                             |
| 21  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | tributyl phosphate                    | 5                             |
|     |                |                               |                               |                                                 |                      |                         |                               | chlorinated paraffin                  | 5                             |
| 22  | "              | "                             | "                             | "                                               | "                    | "                       | "                             | sulfurized fat and oil                | 5                             |
|     |                |                               |                               |                                                 |                      |                         |                               | pentachlorinated fatty ester          | 5                             |
| 23  | "              | "                             | 75                            | "                                               | "                    | "                       | "                             | dioleyl hydrogen phosphite            | 5                             |
|     |                |                               |                               |                                                 |                      |                         |                               | sulfurized fat and oil                | 5                             |
|     |                |                               |                               |                                                 |                      |                         |                               | chlorinated paraffin                  | 5                             |

Table 4

| conventional<br>lubricant | base oil       |                               |                               | extreme-pressure<br>additive                                                            |      |                                     | solid lubricant               |                         |                                     |
|---------------------------|----------------|-------------------------------|-------------------------------|-----------------------------------------------------------------------------------------|------|-------------------------------------|-------------------------------|-------------------------|-------------------------------------|
|                           | kind           | viscosity<br>at 40°C<br>(cSt) | amount of<br>incorp.<br>(wt%) | kind                                                                                    | kind | average<br>particle<br>dia.<br>(μm) | amount of<br>incorp.<br>(wt%) | kind                    | average<br>particle<br>dia.<br>(μm) |
| A                         | mineral oil    | 200                           | 39                            | fatty oil content:<br>43 wt%<br>chlorine content:<br>12 wt%<br>sulfur content:<br>6 wt% | -    | -                                   | -                             | -                       | -                                   |
| B                         | rapeseed oil   | 45                            | 85                            | -                                                                                       | -    | -                                   | -                             | molybdenum<br>disulfide | 5                                   |
| C                         | polybudene oil | 205                           | 80                            | sulfurized fat and<br>oil: 10 wt%                                                       | -    | -                                   | -                             | polyethylene            | 10                                  |

Table 5

| group                                                        | No. | maximum allowable working temp. (°C)               |                                                     |
|--------------------------------------------------------------|-----|----------------------------------------------------|-----------------------------------------------------|
|                                                              |     | forward extrusion working (degree of working: 75%) | backward extrusion working (degree of working: 64%) |
| lubricating oil for plastic working of the present invention | 10  | 350                                                | 240                                                 |
|                                                              | 11  | 350                                                | 190                                                 |
|                                                              | 12  | 330                                                | 195                                                 |
|                                                              | 13  | 350 or higher                                      | 210                                                 |
|                                                              | 14  | 350 or higher                                      | 220                                                 |
|                                                              | 15  | 340                                                | 215                                                 |
|                                                              | 16  | 350 or higher                                      | 180                                                 |
|                                                              | 17  | 340                                                | 200                                                 |
|                                                              | 18  | 345                                                | 200                                                 |
|                                                              | 19  | 350 or higher                                      | 240                                                 |
|                                                              | 20  | 350                                                | 240                                                 |
|                                                              | 21  | 350                                                | 235                                                 |
|                                                              | 22  | 335                                                | 210                                                 |
|                                                              | 23  | 350 or higher                                      | 245                                                 |
| conventional lubricating oil                                 | A   | 80                                                 | 30°C, seizing occurred in working of single piece   |
|                                                              | B   | 30                                                 | "                                                   |
|                                                              | C   | 60                                                 | "                                                   |

EXAMPLES 24 to 39

With respect to lubricating oils for plastic working of the present invention prepared by incorporating a urea lubricant powder as the component A and an extreme-  
5 pressure additive as the component B in base oils, i.e.,  $\alpha$ -olefin oil, neopentyl polyol ester oil, polyphenyl ether oil or fluorosilicone oil as indicated in Table 6, the maximum allowable working temperature was determined by the forward extrusion working method and the backward  
10 extrusion working method under the same conditions as in EXAMPLE 1. The results are shown in Table 7. The lubricating oils for plastic working containing a urea lubricant powder as the component A and at least one member selected from among phosphorus-, sulfur- and  
15 chlorine-based extreme-pressure additives as the component B exhibits an excellent resistance to seizing, regardless of the kind of the base oil.

EXAMPLES 40 to 70

20 A mineral oil having a viscosity of 150 cSt at 40°C was used as the base oil. A urea lubricant powder having an average particle diameter of 90 $\mu$ m produced by using raw materials of the component A as indicated in Table 8 and extreme-pressure additives such as pyrophosphoric  
25 acid, dioleoyl hydrogen phosphite as the component B were incorporated in various amounts in the base oil. The maximum allowable working temperature of the resulting

lubricating oils for plastic working was evaluated. The results are shown in Table 9.

Table 6

| No.                  | component A<br>urea<br>lubricant<br>power (wt%) | base oil             |                               |                               | component B extreme-pressure additive |                               |   |
|----------------------|-------------------------------------------------|----------------------|-------------------------------|-------------------------------|---------------------------------------|-------------------------------|---|
|                      |                                                 | kind                 | viscosity<br>at 40°C<br>(cSt) | amount of<br>incorp.<br>(wt%) | kind                                  | amount of<br>incorp.<br>(wt%) |   |
| 24                   | obtained in<br>EX. 10<br>( 10 )                 | $\alpha$ -olefin oil | 100                           | 80                            | monobutyl phosphate                   | 10                            |   |
| 25                   |                                                 |                      |                               | 80                            | pyrophosphoric acid                   | 10                            |   |
| 26                   |                                                 |                      |                               | 75                            | pyrophosphoric acid                   | 5                             |   |
|                      |                                                 |                      |                               |                               | dioleyl hydrogen phosphate            | 10                            |   |
| 27                   |                                                 |                      |                               |                               | 75                                    | dioleyl hydrogen phosphate    | 5 |
|                      |                                                 |                      |                               |                               |                                       | sulfurized fat and oil        | 5 |
|                      |                                                 |                      |                               | chlorinated paraffin          |                                       | 5                             |   |
| 28                   | neopentyl-<br>polyol<br>ester oil               | 56                   | 80                            | monobutyl phosphate           |                                       | 5                             |   |
| 29                   |                                                 |                      | 80                            | pyrophosphoric acid           | 5                                     |                               |   |
|                      |                                                 |                      | 30                            | 75                            | pyrophosphoric acid                   | 5                             |   |
| 31                   |                                                 |                      |                               | 75                            | dioleyl hydrogen phosphate            | 10                            |   |
|                      |                                                 |                      | dioleyl hydrogen phosphate    |                               | 5                                     |                               |   |
|                      |                                                 |                      | sulfurized fat and oil        |                               | 5                                     |                               |   |
| chlorinated paraffin |                                                 |                      | 5                             |                               |                                       |                               |   |

Table 6 (cont'd)

| No. | component A<br>urea<br>lubricant<br>power (wt%) | base oil                |                               |                               | component B<br>extreme-pressure additive |    |
|-----|-------------------------------------------------|-------------------------|-------------------------------|-------------------------------|------------------------------------------|----|
|     |                                                 | kind                    | viscosity<br>at 40°C<br>(cst) | amount of<br>incorp.<br>(wt%) |                                          |    |
| 32  | ditto                                           | polyphenyl<br>ether oil | 230                           | 80                            | monobutyl phosphate                      | 5  |
| 33  |                                                 |                         |                               | 80                            | pyrophosphoric acid                      | 5  |
| 34  |                                                 |                         |                               | 75                            | pyrophosphoric acid                      | 5  |
|     |                                                 |                         |                               |                               | dioleyl hydrogen phosphate               | 10 |
| 35  |                                                 |                         | 75                            | dioleyl hydrogen phosphate    | 5                                        |    |
|     |                                                 |                         |                               | sulfurized fat and oil        | 5                                        |    |
|     |                                                 |                         |                               | chlorinated paraffin          | 5                                        |    |
| 36  | ditto                                           | fluorosilicone<br>oil   | 200                           | 80                            | monobutyl phosphate                      | 5  |
| 37  |                                                 |                         |                               | 80                            | pyrophosphoric acid                      | 5  |
| 38  |                                                 |                         |                               | 75                            | pyrophosphoric acid                      | 5  |
|     |                                                 |                         |                               |                               | dioleyl hydrogen phosphate               | 10 |
| 39  |                                                 |                         |                               | 75                            | dioleyl hydrogen phosphate               | 5  |
|     |                                                 |                         |                               |                               | sulfurized fat and oil                   | 5  |
|     |                                                 |                         |                               | chlorinated paraffin          | 5                                        |    |

Table 7

| No. | maximum allowable working temp. (°C)                     |                                                           |
|-----|----------------------------------------------------------|-----------------------------------------------------------|
|     | forward extrusion<br>working (degree of<br>working: 75%) | backward extrusion<br>working (degree of<br>working: 75%) |
| 24  | 340                                                      | 235                                                       |
| 25  | 320                                                      | 185                                                       |
| 26  | 350 or higher                                            | 220                                                       |
| 27  | 350 or higher                                            | 240                                                       |
| 28  | 330                                                      | 220                                                       |
| 29  | 320                                                      | 180                                                       |
| 30  | 350                                                      | 225                                                       |
| 31  | 350                                                      | 230                                                       |
| 32  | 350                                                      | 230                                                       |
| 33  | 320                                                      | 210                                                       |
| 34  | 350                                                      | 235                                                       |
| 35  | 350                                                      | 240                                                       |
| 36  | 340                                                      | 235                                                       |
| 37  | 325                                                      | 215                                                       |
| 38  | 350                                                      | 245                                                       |
| 39  | 350                                                      | 235                                                       |

Table 8

| No. | mineral<br>oil<br>(wt%) | raw materials for<br>component A |                      | component A<br>urea<br>lubricant<br>powder (wt%) | component B            |                             | extreme-pressure<br>additive (wt%) |
|-----|-------------------------|----------------------------------|----------------------|--------------------------------------------------|------------------------|-----------------------------|------------------------------------|
|     |                         | amine                            | isocyanate           |                                                  | pyrophosphoric<br>acid | diolylhydrogen<br>phosphite |                                    |
| 40  | 99                      | o-tolidine                       | phenyl<br>isocyanate | 1                                                | 0                      |                             |                                    |
| 41  | 97                      |                                  |                      | 1                                                | 1                      | 1                           |                                    |
| 42  | 96                      |                                  |                      | 2                                                | 2                      |                             |                                    |
| 43  | 96                      |                                  |                      | 2                                                |                        | 2                           |                                    |
| 44  | 96                      |                                  |                      | 2                                                | 1                      | 1                           |                                    |
| 45  | 93                      |                                  |                      | 5                                                | 2                      |                             |                                    |
| 46  | 88                      |                                  |                      | 10                                               | 2                      |                             |                                    |
| 47  | 78                      |                                  |                      | 20                                               | 2                      |                             |                                    |
| 48  | 68                      |                                  |                      | 30                                               | 2                      |                             |                                    |
| 49  | 50                      |                                  |                      | 30                                               | 10                     | 10                          |                                    |
| 50  | 45                      |                                  |                      | 35                                               |                        | 20                          |                                    |
| 51  | 45                      |                                  |                      | 30                                               |                        | 25                          |                                    |
| 52  | 78                      |                                  |                      | 2                                                | 20                     |                             |                                    |
| 53  | 70                      |                                  |                      | 10                                               |                        | 20                          |                                    |
| 54  | 70                      |                                  |                      | 10                                               | 5                      | 15                          |                                    |
| 55  | 72                      |                                  |                      | 15                                               | 3                      | 10                          |                                    |

Table 8 (cont'd)

| No. | mineral oil (wt%) | raw materials for component A |                                                        | component A urea lubricant powder (wt%) | component B         |                           | extreme-pressure additive (wt%) |
|-----|-------------------|-------------------------------|--------------------------------------------------------|-----------------------------------------|---------------------|---------------------------|---------------------------------|
|     |                   | amine                         | isocyanate                                             |                                         | pyrophosphoric acid | dioleylhydrogen phosphite |                                 |
| 56  | 96                | p-phenylene-diamine           | phenyl isocyanate                                      | 2                                       | 2                   |                           |                                 |
| 57  | 93                |                               |                                                        | 5                                       | 2                   |                           |                                 |
| 58  | 70                |                               |                                                        | 10                                      | 5                   | 15                        |                                 |
| 59  | 96                | p-chloro-aniline              | tolylene diisocyanate                                  | 2                                       | 2                   |                           |                                 |
| 60  | 93                |                               |                                                        | 5                                       | 2                   |                           |                                 |
| 61  | 70                |                               |                                                        | 10                                      | 5                   | 15                        |                                 |
| 62  | 96                | aniline                       | "                                                      | 2                                       | 2                   |                           |                                 |
| 63  | 93                |                               |                                                        | 5                                       | 2                   |                           |                                 |
| 64  | 70                |                               |                                                        | 10                                      | 5                   | 15                        |                                 |
| 65  | 96                | ethylenediamine oleylamine    | "                                                      | 2                                       | 2                   |                           |                                 |
| 66  | 93                |                               |                                                        | 5                                       | 2                   |                           |                                 |
| 67  | 70                |                               |                                                        | 10                                      | 5                   | 15                        |                                 |
| 68  | 96                | "                             | 2,4-tolylene diisocyanate<br>2,6-tolylene diisocyanate | 2                                       | 2                   |                           |                                 |
| 69  | 93                |                               |                                                        | 5                                       | 2                   |                           |                                 |
| 70  | 70                |                               |                                                        | 10                                      | 5                   | 15                        |                                 |

Table 9

| No. | maximum allowable working temp. (°C)                     |                                                           |
|-----|----------------------------------------------------------|-----------------------------------------------------------|
|     | forward extrusion<br>working (degree of<br>working: 75%) | backward extrusion<br>working (degree of<br>working: 64%) |
| 40  | 55                                                       | 30                                                        |
| 41  | 60                                                       | 30                                                        |
| 42  | 105                                                      | 45                                                        |
| 43  | 105                                                      | 40                                                        |
| 44  | 100                                                      | 45                                                        |
| 45  | 280                                                      | 110                                                       |
| 46  | 340                                                      | 230                                                       |
| 47  | 350                                                      | 240                                                       |
| 48  | 350                                                      | 245                                                       |
| 49  | 350                                                      | 245                                                       |
| 50  | 350                                                      | 245                                                       |
| 51  | 350                                                      | 245                                                       |
| 52  | 60                                                       | 40                                                        |
| 53  | 300                                                      | 230                                                       |
| 54  | 350                                                      | 240                                                       |
| 55  | 350                                                      | 240                                                       |
| 56  | 70                                                       | 40                                                        |
| 57  | 290                                                      | 105                                                       |
| 58  | 340                                                      | 235                                                       |
| 59  | 65                                                       | 40                                                        |
| 60  | 295                                                      | 70                                                        |

Table 9 (cont'd)

| No. | maximum allowable working temp. (°C)                     |                                                           |
|-----|----------------------------------------------------------|-----------------------------------------------------------|
|     | forward extrusion<br>working (degree of<br>working: 75%) | backward extrusion<br>working (degree of<br>working: 64%) |
| 61  | 350                                                      | 210                                                       |
| 62  | 60                                                       | 35                                                        |
| 63  | 260                                                      | 80                                                        |
| 64  | 330                                                      | 220                                                       |
| 65  | 70                                                       | 40                                                        |
| 66  | 250                                                      | 65                                                        |
| 67  | 320                                                      | 215                                                       |
| 68  | 55                                                       | 40                                                        |
| 69  | 230                                                      | 60                                                        |
| 70  | 300                                                      | 200                                                       |

EXAMPLES 71 to 78

A mineral oil having a viscosity of 150 cSt at 40°C was used as the base oil. A urea lubricant powder, i.e., component A, produced by using the same raw materials as in EXAMPLE 1, i.e., o-tolidine and phenyl isocyanate was incorporated in the base oil in varied average particle diameter in the range of 0.2 to 800 $\mu$ m as indicated in Table 10. The maximum allowable working temperature of the resulting lubricating oil for plastic working was evaluated. The results are shown in Table 10.

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Table 10

| No. | base oil    |                         | component A             |                                        |       | urea lubricant powder |                            | component B             |                     | extreme-pressure additive |                         | maximum allowable working temp. (°C)               |                                                     |
|-----|-------------|-------------------------|-------------------------|----------------------------------------|-------|-----------------------|----------------------------|-------------------------|---------------------|---------------------------|-------------------------|----------------------------------------------------|-----------------------------------------------------|
|     | kind        | viscosity at 40°C (cSt) | amount of incorp. (wt%) | raw materials for production lubricant | amine | isocyanate            | average particle dia. (µm) | amount of incorp. (wt%) | kind                | amount of incorp. (wt%)   | amount of incorp. (wt%) | forward extrusion working (degree of working: 75%) | backward extrusion working (degree of working: 64%) |
| 71  | mineral oil | 150                     | 70                      | o-tolidine                             |       | phenyl isocyanate     | 0.2                        | 10                      | pyrophosphoric acid | 5                         |                         | 350                                                | 35                                                  |
| 72  | "           | "                       | "                       | "                                      | "     | "                     | 0.3                        | "                       | "                   | "                         |                         | 350                                                | 40                                                  |
| 73  | "           | "                       | "                       | "                                      | "     | "                     | 0.5                        | "                       | "                   | "                         |                         | 350                                                | 55                                                  |
| 74  | "           | "                       | "                       | "                                      | "     | "                     | 5.0                        | "                       | "                   | "                         |                         | 350                                                | 70                                                  |
| 75  | "           | "                       | "                       | "                                      | "     | "                     | 50                         | "                       | "                   | "                         |                         | 350                                                | 205                                                 |
| 76  | "           | "                       | "                       | "                                      | "     | "                     | 200                        | "                       | "                   | "                         |                         | 350                                                | 245                                                 |
| 77  | "           | "                       | "                       | "                                      | "     | "                     | 500                        | "                       | "                   | "                         |                         | 350                                                | 245                                                 |
| 78  | "           | "                       | "                       | "                                      | "     | "                     | 800                        | "                       | "                   | "                         |                         | 345                                                | 245                                                 |

EXAMPLE 79

The lubricating oil as obtained in EXAMPLE 1 was applied on the surface of JIS A2218 aluminum alloy material having a shape as shown in FIG. 6 by spraying. The material was inserted into a mold and subjected to cold forging in such a state that the temperature of both the alloy and the mold were ordinary one to form 500 cylinders for a video tape recorder having a shape as shown in FIG. 7. A coating, i.e., a product of a reaction of the lubricant oil with the substrate, is formed on the surface of the material after working, and the surface was like a mirror.

In the present example, one or both of the internal and external peripheral surfaces 11, 12 on which a tape is traveled is often cut and polished. Alternatively, the cylinder may be used as it is without removing the coating formed by a reaction between the lubricating oil for plastic working and the substrate. When an oval through-hole is provided at the bottom of the internal peripheral surface 14, the external peripheral surface is cut and polished to attain roundness of the external peripheral surface. When a groove is provided at the step portion 13, the entire portion of the step is cut and polished.

However, the cylinder may be used as it is without removing the coating formed by a reaction between the lubricating oil for plastic working and the substrate. The worked material itself has a mirror surface.

EXAMPLE 80

The lubricating oil as obtained in EXAMPLE 1 was applied on the surface of A3003 aluminum alloy material having a diameter of 50 mm and a length of 45 mm. The material was inserted into a mold and subjected to cold forging in such a state that the temperature of both the alloy and the mold were ordinary one to form a vessel as shown in FIG. 8 having an external diameter of 50 mm, an internal diameter of 40 mm and a length of 100 mm. A coating i.e., a product of a reaction of the lubricant oil with the substrate, is formed on the surface of the material after working, and the surface was like a mirror.

In the present invention, a cup-like article as shown in FIG. 8 was formed from a block. The article having the worked internal and external peripheral surfaces can be used as it is. Both of the internal and external peripheral surfaces were like a mirror. The bottom was cut to form a cylinder. A coating, i.e., a reaction product, is formed on the surface of the material after working. Only the external peripheral surface may be cut and polished.

Further, it is possible to directly form a cylinder by subjecting a pipe shaped material to plastic working. Therefore, the formed product is used as it is after cutting only the edge face. The article can be formed by a single-step working or two-step working in which a further working is conducted in the smaller degree of

working than that in the first step. The two-step working leads to a further improved mirror surface. The second working is conducted without addition of the lubricating oil.

5

#### EXAMPLE 81

The lubricating oil as obtained in EXAMPLE 1 was applied on the surface of A2218 aluminum alloy material having a diameter of 40.4 mm and a length of 20 mm by the immersion method. The material was inserted into a mold and subjected to cold forging in such a state that the temperature of both the alloy and the mold was ordinary one to form a pinion having a shape as shown in FIG. 9. A coating, i.e., a product of a reaction of the lubricant oil with the substrate, is formed on the surface of the material after working, and the surface was like a mirror.

In the present example, the coating which has been formed during the working of the curved portions of the teeth 22 remains on the article. However, the top of the teeth 22 may be cut and polished. The internal peripheral surface 21 is left intact. Numeral 24 designates a through-hole portion formed by cutting. The surface designated by numeral 25 may be left intact or may be subjected to cutting treatment. The bottom surface 23 is left as it is.

As is apparent from the foregoing, the lubricating oil of the present invention comprising a base oil such

as a mineral oil or synthetic oil or a mixture thereof  
and a diurea or polyurea incorporated therein forms a  
lubricating coating having excellent thermal resistance  
and loading resistance on the frictional surface during  
5 working by simply applying it on the surface of a material  
or a mold and, therefore, not only effectively prevent  
occurrence of seizing but also greatly contributes to an  
improvement in the service life of tools such as a mold,  
enhancement of productivity and reduction in production  
10 cost.

Further, the plastic working product of the present  
invention has a coating comprising the above-mentioned  
lubricating oil on its surface which particularly exhibits  
an excellent anticorrosive effect for steel stocks, so  
15 that a plastic working product having excellent corrosion  
resistance is advantageously provided.

CLAIMS

1. A lubricating oil for plastic working comprising a lubricating oil and a powder of a compound having a urea bond dispersed and incorporated in said lubricating oil.
- 5 2. A lubricating oil for plastic working according to claim 1 wherein said powder has a particle diameter of 35 to 500  $\mu\text{m}$ .
3. A lubricating oil for plastic working according to claim 1 or claim 2, wherein said powder is incorporated  
10 in said lubricating oil in an amount of 1.5 to 25% by weight.
4. A lubricating oil for plastic working according to any one of claims 1 to 3 which contains, as well as (A) said powder of a compound having a urea  
15 bond,  
(B) at least one extreme-pressure additive selected from:
  - (1) condensed phosphoric acid,
  - (2) phosphite and phosphate esters,
  - 20 (3) organic sulfur compounds, and
  - (4) organic chlorine compounds.

5. A lubricating oil for plastic working according to any one of claims 1 to 4 wherein said powder is coated with a wax.

6. A plastic working product comprising a molding,  
5 wherein said molding has on its surface a coating of a lubricating oil according to any one of the preceding claims.

7. A cylinder for a video tape recorder produced by plastic working using a lubricating oil for plastic  
10 working, wherein said cylinder has on its surface a coating of said lubricating oil which oil is according to any one of claims 1 to 5.

8. A photosensitive drum for electrophotography produced by plastic working using a lubricating oil  
15 for plastic working, wherein said photosensitive drum has on its surface a coating of said lubricating oil which oil is according to any one of claims 1 to 5.

9. A pinion for an automobile or other machine produced by plastic working using a lubricating oil  
20 for plastic working, wherein said pinion has on its surface a coating of said lubricating oil which oil is according to any one of claims 1 to 5.

FIG. 1

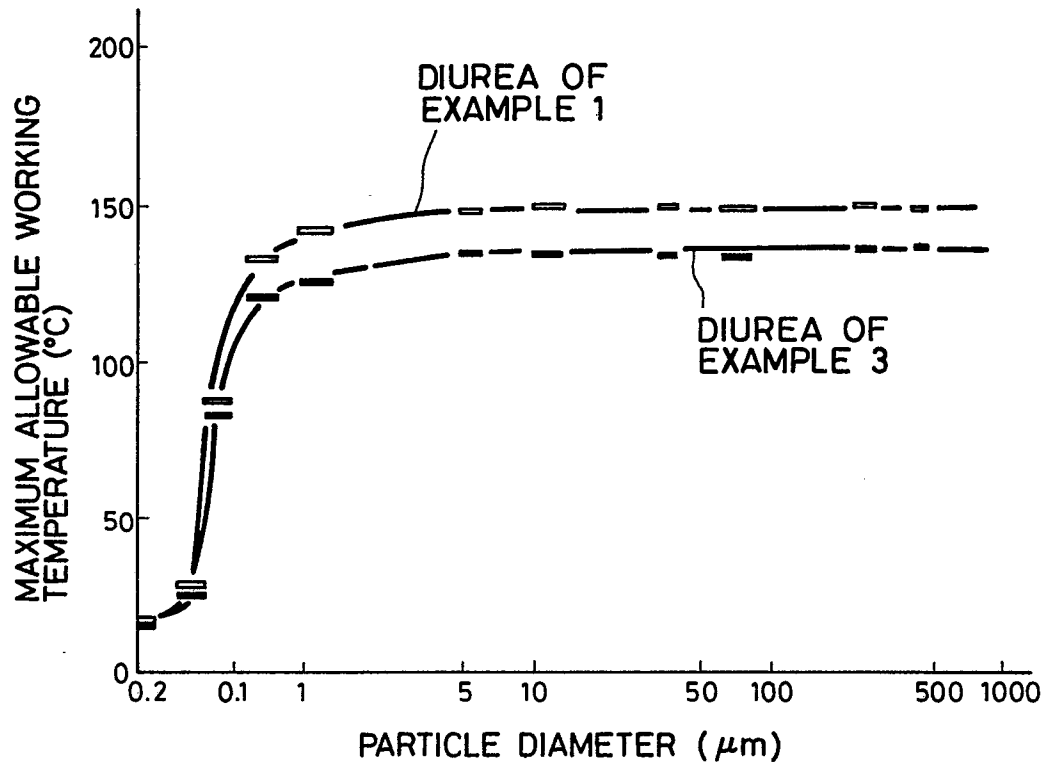


FIG. 2

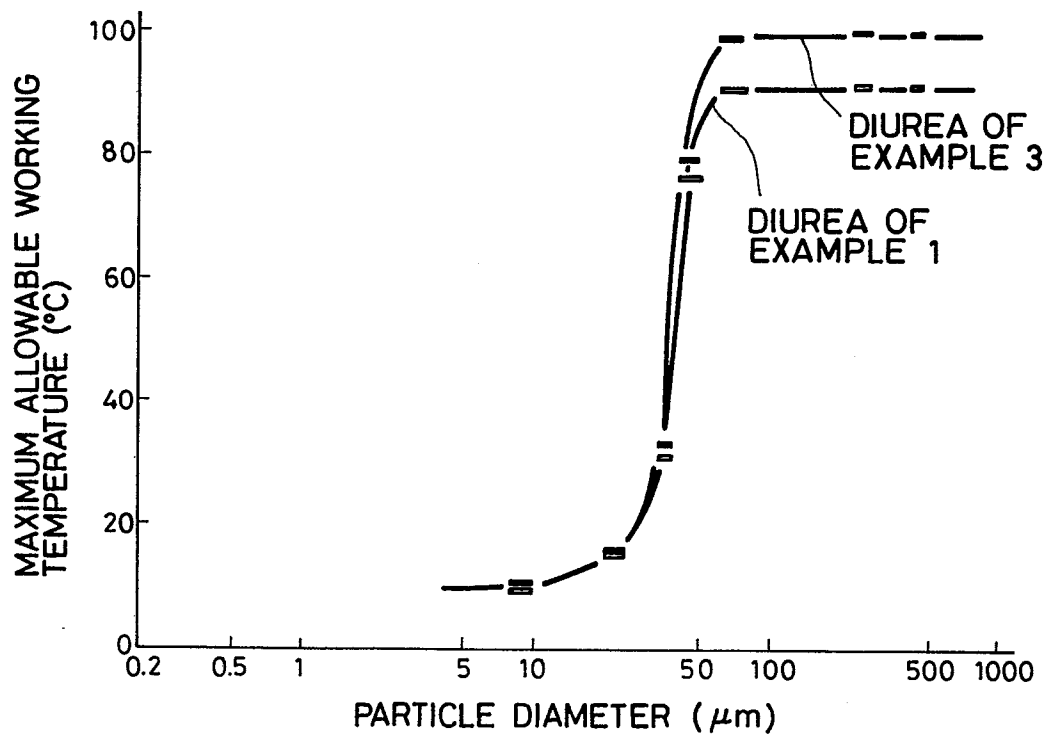


FIG. 3

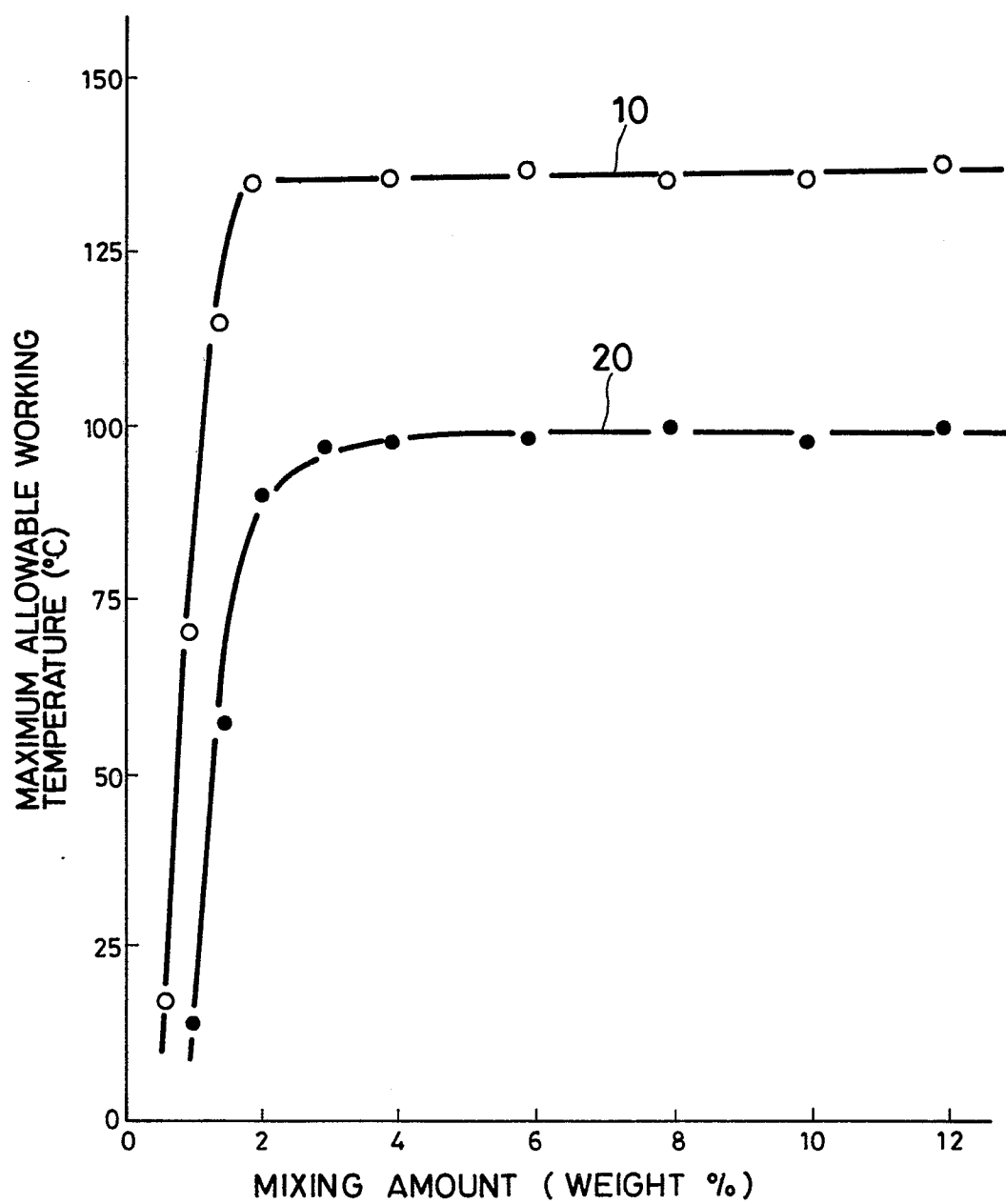


FIG. 4(a)

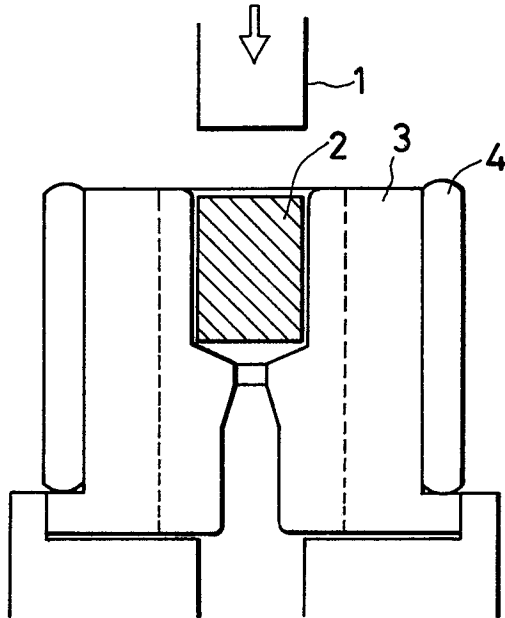


FIG. 4(b)

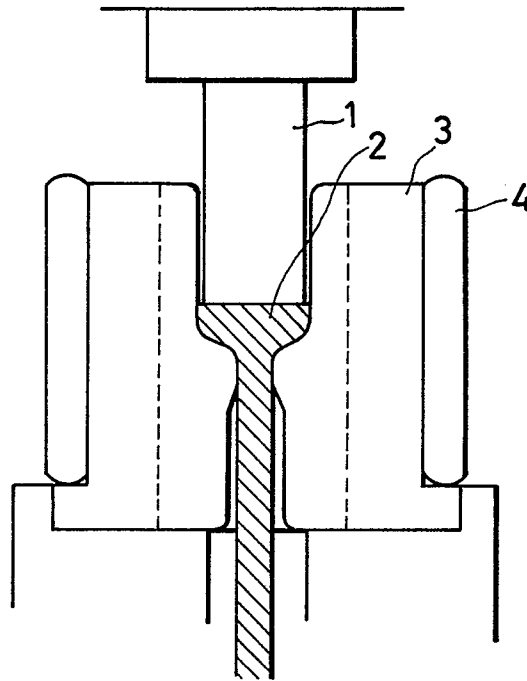


FIG. 5(a)

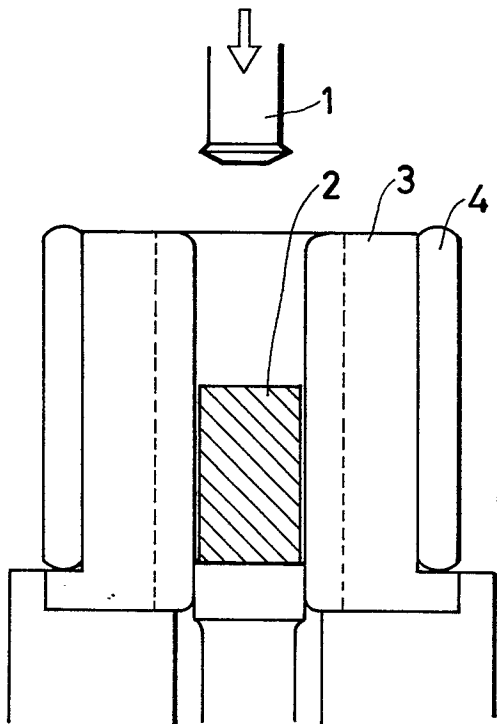
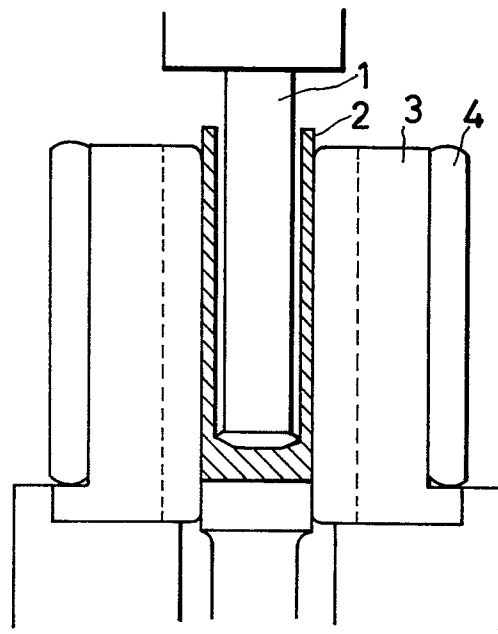
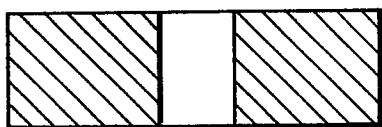
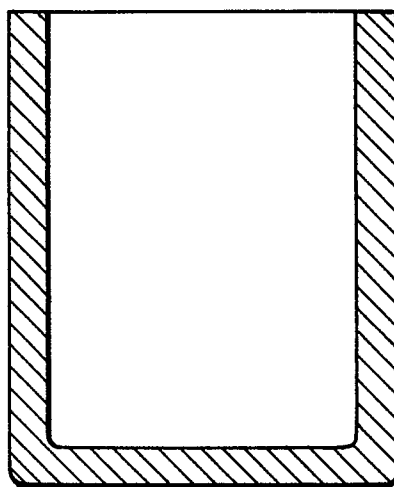
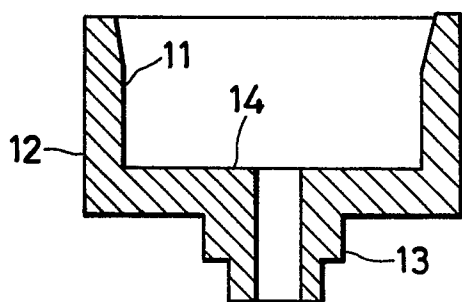


FIG. 5(b)



**FIG. 6****FIG. 8****FIG. 7****FIG. 9**