(54) Title: AQUEOUS LUBRICANT USED FOR PLASTIC WORKING OF METALLIC MATERIAL AND METHOD OF LUBRICATIVE FILM PROCESSING

(57) Abrégé_Abstract:
An aqueous lubricant used for plastic working of metallic material which comprises (A) a water soluble inorganic salt, (B) lubricative agent selected from molybdenum disulfide and graphite and (C) wax, wherein the components are dissolved or dispersed in water,
(57) Abrégé(suite)/Abstract(continued):

and wherein a concentration ratio (weight ratio) of (B)/(A) is in the range of 1.0-5.0 and (C)/(A) is 0.1-1.0. And a method of lubricative film processing on a metallic material, in that the lubricative film formed by applying the aqueous lubricant is in a dried weight of 0.5-40g/m². A water soluble inorganic salt (A) is preferably selected from the group consisting of a sulfate, a silicate, a borate, a molybdate and a tungstate. The wax (C) is preferably a natural wax or a synthetic wax which is dispersed in water and has a melting point of 70-150°C. The aqueous lubricant can be used for imparting excellent lubricity with ease to the surface of a metal having no chemical conversion layer formed thereon.
ABSTRACT

An aqueous lubricant used for plastic working of metallic material which comprises (A) a water soluble inorganic salt, (B) lubricative agent selected from molybdenum disulfide and graphite and (C) wax, wherein the components are dissolved or dispersed in water, and wherein a concentration ratio (weight ratio) of (B)/(A) is in the range of 1.0-5.0 and (C)/(A) is 0.1-1.0. And a method of lubricative film processing on a metallic material, in that the lubricative film formed by applying the aqueous lubricant is in a dried weight of 0.5-40g/m². A water soluble inorganic salt (A) is preferably selected from the group consisting of a sulfate, a silicate, a borate, a molybdate and a tungstate. The wax (C) is preferably a natural wax or a synthetic wax which is dispersed in water and has a melting point of 70-150°C. The aqueous lubricant can be used for imparting excellent lubricity with ease to the surface of a metal having no chemical conversion layer formed thereon.
AQUEOUS LUBRICANT USED FOR PLASTIC WORKING OF METALLIC MATERIAL AND METHOD OF LUBRICATIVE FILM PROCESSING

FIELD OF THE INVENTION

This invention relates to an aqueous lubricant used for plastic working of metallic material such as iron and steel, stainless steel, titanium, aluminum and others, wherein the surface of the metallic material has not been given any chemical conversion treatment. Also, it relates to a process of using the lubricant.

Being described in more detail, this invention relates to an aqueous lubricant used for producing a lubricative film suitable for plastic deforming work such as forging, wire drawing, tube drawing and others, on the surface of the metallic materials such as iron and steel, stainless steel, titanium, aluminum and others, wherein the surface of the metallic material has not been subjected to any chemical conversion treatment.

BACKGROUND ART

When cold plastic working are performed on the metallic material such as iron and steel, stainless steel and others, lubricative film are generally provided on the surface of the metallic material in order to prevent burning defects and galling defects which are arisen by metallic contact between the metallic material and tool.

Regarding the lubricative film being provided on the
metal surface, there are lubricative film in which lubricative agent is made to adhere physically on the metal surface and other type of lubricative film in which chemical conversion layer are produced on the metal surface previously by chemical conversion treatment of the metallic material and then lubricative agent are applied on the chemical conversion layer.

The lubricative agent being adhered physically on the metal surface are used generally for cold working of slight amount of reduction since adhesive power of these are inferior than the adhesive power of the lubricative agent being applied on the chemical conversion layer.

In using the chemical conversion film, phosphate film or oxalate film are provided on the metal surface, which has a role as a carrier for the lubricative agent being applied on it. The lubricative film of this type are constructed by 2 layers, the carrier layer and the lubricative agent layer, and shows very excellent resistance against burning defect of the metallic material. And are used in a wide range of the cold working such as wire drawing, tube drawing, forging and others. And besides in the field of the cold working of heavy amount of reduction, it is widely used to provide a phosphate film or oxalate film, and a lubricative agent are applied on that.

The lubricative agent applied on the chemical conversion layer may be divided into two groups in terms of the usage. The first group includes a lubricative agent to
be mechanically adhered onto the chemical conversion layer and the second group includes a lubricative agent which reacts with the chemical conversion layer.

The first group of lubricative agent includes those being prepared by using mineral oil, vegetable oil or synthetic oil as base oil and containing an extreme pressure additive in the base oil, also includes other one being prepared by dissolving a solid lubricative agent, such as graphite and molybdenum disulfide, together with a binder component into the water. These are adhered and then dried.

These lubricative agent of the first group may have advantages of easy for handling the solution since they may be used simply by means of spray coating or dipping coating. However, as they have just a low lubricative properties, they tend to be used for a case where slight amount of deformation of the metallic material is required.

On the other hand, in the second group of the lubricative agent, a reactive soap such as sodium stearate is sued for a cold working where high lubricative property is required. The reactive soap reacts with the chemical conversion layer and provides a layer of high lubricative property.

However, since the reactive soap cause a chemical reaction, composition control of the solution, temperature control for the chemical reaction and the renewal control
of the deteriorated solution by discharging of the waste from the solution, etc, become very important during the process.

Recently, it is a big issue to reduce waste products from the industries for global environmental protection. And therefore, new lubricative agent and new lubricative process which do not discharge waste products have been highly desired. Also, some new processes which enable to simplify the complex control of the process and the solution in the above explained second group have been further desired.

In order to solve problems as described above, JP52-20967A, wherein a lubricant composition containing water soluble polymer or its aqueous emulsion as the base component, a solid lubricant and a film-forming agent has been disclosed. However, no composition which has the same degree of preferable effect as in the conventional process of using a chemical conversion layer has been obtained.

In order to solve the problems as described above, another prior art of JP10-008085A has been disclosed. This prior art relates to an aqueous lubricant used for plastic working of metallic material in which (A) water soluble inorganic salt, (B) solid lubricative agent, (C) at least one oil selected from a group consisting of mineral oil, animal oil, vegetable oil and synthetic oil, (D) surface active agent and (E) water are well dispersed and emulsified homogeneously. However, the lubricant according
to this prior art is too unstable to use in an industry since it has to keep to emulsify the oil component, and is not showing a stable properties.

As another prior art, an invention of JP2000-063880A can be cited. This prior art is directed to a lubricant used for plastic working of metallic material comprising (A) synthetic resin, (B) water soluble inorganic salt and water, wherein the ratio of (B)/(A) by weight in solid state is in a range from 0. 25/1 to 9/1 and the synthetic resin is kept dissolved or dispersed in the composition. However, this composition is also not stable to show a high lubricative properties in cold working of heavy amount of reduction, since its main component is the synthetic resin.

Therefore, it is an object of this invention to provide an aqueous lubricant used for plastic working of metallic material and a method of lubricative film processing, in which the metallic material has not been subjected to any chemical conversion treatment, and in which the problems existing in the conventional process may be solved and the problems in the global environmental protection may also be improved and is applicable to many sorts of metallic materials.

DISCLOSURE OF THE INVENTION

The inventors have investigated for solving the problems described above and have found that the excellent lubricative properties can be obtained by the aqueous solution containing water soluble inorganic salt, lubricative agent
being selected from molybdenum disulphide and graphite, and wax at the specific ratio. Further, they have found out a method of lubricative film processing on the metal surface in saving the treating energy and in saving the treating space.

Namely, the present invention is an aqueous lubricant used for plastic working of metallic material which contains (A) water soluble inorganic salt being selected from the group consisting of sulphate, silicate, borate, molybdate and tungstate, (B) one or more than one lubricative agent being selected from the group consisting of molybdenum disulphide and graphite, and (C) wax, and these components are dissolved in water and weight ratio of (B)/(A) in solid state is in the range of 1.0 to 5.0 and weight ratio of (C) 1 (A) in solid state is in the range of 0.1 to 1.0, and which does not contain any other synthetic resin than the wax (C).

It is preferable that (A) as above is one or more water soluble inorganic salt being selected from a group of sulfate, silicate, borate, molybdate and tungstate, and it is preferable that wax as above is water dispersed natural wax or synthetic wax having melting point between 70-150°C.

Also, the present invention is a method of processing of the lubrication film of 0.5-40g/m² as adherent weight on the surface of the metallic material wherein the aqueous lubricant of above is applied to the cleaned surface of the metallic material and is then dried. It is preferable that the surface of the metallic material is previously cleaned by one or more process selected from a group of shot blasting, sand blasting, alkaline degreasing and acid cleaning, and also preferable that the aqueous lubricant is applied on the
surface of the metallic material after the metallic material is heated to 60-100°C.

**BRIEF DESCRIPTION OF DRAWINGS**

Fig 1: Illustrative drawing of rear punching test.
   Fig 1(A): Illustrates the sample before the punching test.
   Fig 1(B): Illustrates the sample during the punching test.
   Fig 1(C): Illustrates the sample after the punching test.

Fig 2: Illustrative drawing of spike test.
   Fig 2(A): Illustrates a first part of the test where a rod sample is set on top of a die.
   Fig 2(B): Illustrates a second part of the test where the rod sample is pressed and a portion is forced to move into the die.

**BEST MODES FOR CARRYING OUT THE INVENTION**

Now, the present invention is explained further in detail. The water soluble inorganic salt (A) used in the aqueous lubricant of the invention is contained in order to give hardness and strength to the coating film. For this purpose, it is required to have a property to be uniformly dissolved in the aqueous solution and to form a strong lubricative film after drying.
As the inorganic salt giving such property, it is preferable to use at least one selected from a group consisting of sulfate, silicate, borate, molybdate and tungstate. As the examples for the inorganic salt described above, sodium sulfate, potassium sulfate, potassium silicate, sodium borate (sodium tetraborate), potassium borate (potassium tetraborate), ammonium borate (ammonium tetraborate), ammonium molybdate, sodium molybdate and sodium tungstate may be given. Any of these salts may be used either alone or in combination of 2 or more salts.

In the present invention one or more than one of the lubricative agent (B) being selected from molybdenum
disulphide and graphite are used in order to enhance the lubricative properties. They are contained in a form of being dispersed, and the known surfactant may be used when necessary.

The (B)/(A), namely the weight ratio in solid state of the water soluble inorganic salt (A) and the lubricative agent (B), is preferable to be in a range of 1.05.0. And is more preferable to be 2.04.0. When the ratio is less than 1.0, sliding properties of the lubricative film are decreased and not preferable. However, when the ratio exceeds 5.0, the aqueous lubricant become unstable and is not preferable.

As wax (C), it is preferable to use a natural wax or a synthetic wax, though there is no specific limitation in its chemical structure and the type. The wax may melt by a heat generated during the plastic deformation of the metallic material thereby improve the lubricative property of the coating layer. For this reason, it is preferable to use those having a melting point in a range of 70-150°C and being stable in aqueous lubricant and those not to weaken the strength of the lubricative film so as to perform the preferable lubrication from the early stage of the plastic working.

The practical examples for the wax may include paraffin wax, micro crystalline wax, petrolatum wax, fisher-tropsch wax, polyethylene wax, polypropylene wax, carnauba wax, montane wax and the like. These waxes are
preferably combined with another component and contained in a form of water dispersion or water emulsion in the aqueous lubricant of the invention.

The \((C)/(A)\), namely the weight ratio in solid state of water soluble inorganic salt \((A)\) and the wax \((C)\) is preferably in a range of 1-1.0, and more preferably in a range of 0.2-0.8. When the ratio is less than 0.1, sliding property of the lubricative film may be insufficient, while the adhesive performance of the coating layer may be insufficient when the ratio is more than 1.0.

It is still possible to add further another oil or another solid lubricative matter to the aqueous lubricant of this invention in cold working with heavy amount of deformation.

When a surface active agent is required for dispersing the lubricative matter and the wax in the aqueous lubricant, any surface active agent of nonionic, anionic, amphoteric and cationic type may be used. Although being not limited, the nonionic surface active agent may include polyoxyethylene alkyle ether, polyoxyalkylene(ethylene and/or propylene) alkyl phenyle ether, polyoxyethylene alkyl ester comprising polyethylene glycol(or ethylene oxide) and higher fatty acid (C12-C18, for example), polyoxyethylene sorbitan alkyl ester comprising sorbitan, polyethylene glycol and higher fatty acid (C12-C18, for example). Although being not limited, the anionic surface active agent may include fatty acid ester salts, sulfuric acid ester salt,
sulfonate salt, phosphoric acid ester salt, and
dithiophosphoric acid ester salt. Although being not limited,
the amphoteric surface active agent may include carboxylates
either in amino acid configuration or in betaine
configuration, sulfuric acid ester salt, sulfonate salt,
phosphoric acid ester salt.

Although being not limited, the cationic surface
active agent may include amine salt of fatty acid,
quaternary ammonium salt and the like.

Each of these surface active agent may be used
either alone or in combination of two or more of them.

Aqueous lubricant of the present invention may
further be applied as a lubricant for cold working (wire
drawing, tube drawing, forging, etc) when the metallic
materials of iron and steel, stainless steel, copper or
copper alloy, aluminum or aluminum alloy, titanium or
titanium alloy are already coated by known process of
forming the phosphate layer (zinc phosphate, manganese
phosphate, iron phosphate, tin phosphate, etc), oxalate
layer (iron oxalate, etc), cryolite and calcium
aluminate layer.

Shape of the metallic material is not especially
limited, and not only bar and block but also shaped
product being produced by hot forging (gear, shaft, etc)
may be used.
According to a method of the lubricative film processing in this invention, a purified surface of the metallic material is made to contact with the aforementioned aqueous lubricant and then dried, and produce the lubricative film of 0.5-40g/ml on the surface of the metallic material. Thus the processing of the lubricative film of the invention is non-reactive type. The amount of the lubricative film produced on the surface of the metal may be adjusted according to the degree of deformation of the plastic cold working. And it is more preferable to be in a range of 2-20g/m².

When it is less than 0.5g/m², the lubricity becomes insufficient. When more than 40g/m², although special problems may not arise in lubricity, dregs may appear in the working and the cavity provided on the surface of the tool may be crammed by arisen dregs. The amount of the lubricative film may be calculated from the surface area of the metallic material and the weight difference before and after the treatment.

The weight concentration of the components are adjusted in order to control the amount of the lubricative film as above. In many cases, treatment solution may be obtained by diluting the concentrated aqueous lubricant by water. The type of the water used for this dilution is not limited, but deionized water or distilled water are preferable.
In the processing of the lubricative film of the invention, surface cleaning of the metallic material is preferable to be carried out by one or more cleaning steps being selected from shot blasting, sand blasting, alkali degreasing and acid cleaning. The main purpose of these cleaning is to remove a oxide scale being grown in the annealing or to remove a contamination of oil or others.

Recently, the reduction of the disposal of the waste water has been desired from the environmental point of view. In this invention, waste water may be possible to decrease to zero, for example, by shot blasting for cleaning the surface and by producing the lubricative film using the aqueous lubricant of the invention.

There are no specific limitation in the method of applying the aqueous lubricant of the invention to the surface of the metallic material. And dipping method, flow coat method, spray method and other method can be used. The application is sufficient when the surface is sufficiently covered by the aqueous lubricant, and there is no restriction in applying time.

After the application, it is necessary that the aqueous lubricant is to be dried. Drying may be done by keeping it under the ordinary temperature, and it may also be preferable by keeping it at 60-150°C for 10-60 minutes.

It is preferable that the aqueous lubricant is applied after heating the metallic material to 60-100°C, in
order to increase the drying efficiency. Also, it is preferable to apply the aqueous lubricant after being heated to 50-90°C.

Thus, drying efficiency may be much improved and the loss of heat energy may be much decreased.

EXAMPLES

The advantageous effect of this invention will be explained more practically by showing embodiment examples and comparative examples.

(Sample for rear punching test)

Serious of steel rod samples of JIS S45C being spherodizing annealed, obtained in the market, having a diameter of 30mm and having a serious of heights in 18-40mm as shown in Fig(A) in which height of each rod are different in 2mm each other.

(Sample for spike test)

Steel rod samples of JIS S45C being spherodizing annealed, obtained in the market and having a diameter of 25mm and having a height of 30mm.

(Treating Process)
• Process A

(1) Degreasing : using degreasing agent on the market (FINE CLEANER® 4360, by Nihon Parkerizing Co., Ltd),
concentration: 20g/L, temperature: 60°C, dipping time: 10 minutes.
(2) Washing: by tap water, 60°C, dipping for 30 sec.
(3) Lubricating treatment: contacting with lubricant, at 60°C, dipping for 10 sec.
(4) Drying: 80°C, for 3 min.
   • Process B
(1) Shot blasting: Particle diameter: 0.5mm, treating for 5 min.
(2) Washing: by tap water, 90°C, dipping for 90 sec.
(3) Lubricating treatment: contacting with lubricant at 70°C, dipping for 5 sec.
(4) Drying: room temperature (air blow), for 3 min.

(Rear Punching Test) --- Fig. 1

Series of steel rod samples in Fig. 1 (A) are cold worked by 200 ton crank press in Fig. 1 (B) to produce series of cup shaped products shown in Fig. 1 (C). In each punching, 10mm of bottom end was left, and the reduction of the sectional area was 50%. The defects on the inner surface of cup are inspected, and the maximum depth (Zmm) of cup for which no defects are observed are shown as punch depth (mm) in Table 1. In this test, die material is JIS SRDII, punch material is JIS HAP40, punch diameter is 21.21mm, punching is 30 stroke/min.

(Spike Test) --- Fig. 2
Spike test has been carried out in the same way as shown in JP5-7969A.

Die(1) has an inner surface of the funnel like shape. Rod sample (2) are set on the top of the die (1) as in Fig. 2 (A), then being pressed and the bottom of the sample(2) are forced to move into the funnel hole of the die (1) as shown in Fig.2 (B). By this process, spike having the shape corresponding to the funnel are produced. The height of the formed spike are shown as spike height in Table 1. The lubricating is excellent when the spike has a large spike height.

(Embodiment example 1)

Aqueous lubricant 1 as below (containing 1 wt % of nonionic surfactant for dispersion) was used and treated in Process A above.

Aqueous lubricant 1

- water soluble inorganic salt : sodium tetraborate,
- lubricative agent : molybdenum disulfide
- wax : polyethylene wax
- ratio (B/A) : 3.0 ratio
- (C/A) : 0.4 amount of produced film,
- g/m² : 15

(Embodiment example 2)

Aqueous lubricant 2 as below (containing 1 wt % of nonionic surfactant for dispersion) was used in Process B above.

Aqueous lubricant 2

- water soluble inorganic salt : sodium tetraborate
- lubricative agent : graphite
wax : polyethylene wax
ratio (B/A) : 2.0
ratio (C/A) : 0.8
amount of produced film, g/m² : 15

(Embodiment example 3)

Aqueous lubricant 3 as below (containing 1 wt % of nonionic surfactant for dispersion) was used in Process A above.

Aqueous lubricant 3
water soluble inorganic salt : sodium silicate
lubricative agent : graphite
wax : polyethylene wax
ratio (B/A) : 1.0
ratio (C/A) : 1.0
amount of produced film, g/m² : 15

(Embodiment example 4)

Aqueous lubricant 4 as below (containing 1 wt % of nonionic surfactant for dispersion) was used in Process A above.

Aqueous lubricant 4
water soluble inorganic salt : sodium tungstate,
lubricative agent : molybdenum disulfide
wax : paraffin wax
ratio (B/A) : 4.0
ratio (C/A) : 0.1
amount of produced film : g/m² : 15

(Embodiment example 5)

Aqueous lubricant 5 as below (containing 1 wt % of nonionic surfactant for dispersion) was used in Process B above.
Aqueous lubricant 5
   water soluble inorganic salt : potassium sulfate
   lubricative agent : molybdenum disulfide
   wax : paraffin wax
   ratio (B/A) : 3.0
   ratio (C/A) : 0.5
   amount of produced film, g/m² : 15
(Comparative example 1)

Aqueous lubricant 6 as below (containing 1 wt % of nonionic surfactant for dispersion) was used in Process A above.

Aqueous lubricant 6
   water soluble inorganic salt : potassium sulfate
   wax : paraffin wax
   ratio (C/A) : 0.1
   amount of the produced film, g/m² : 10
(Comparative example 2)

Aqueous lubricant 7 as below (containing 1 wt % of nonionic surfactant for dispersion) was used in treating process B above.

Aqueous lubricant 7
   water soluble inorganic salt : potassium sulfate
   lubricative agent : molybdenum disulfide
   ratio (B/A) : 0.5
   amount of produced film, g/m² : 15
(Comparative example 3)

Treatment was carried out in Process C as below.
   • Process C
(1) Degreasing: using degreasing agent on the market (FINE CLEANER® 4360, by Nihon Parkerizing Co., Ltd), concentration 20g/L, temperature: 60°C, dipping time: 10 min

(2) Washing by tap water, room temperature, dipping for 30 sec.

(3) Chemical conversion treatment: using chemical conversion agent containing zinc phosphate obtained in the market (PALBOND® 181X, by Nihon Parkerizing Co., Ltd), concentration: 90g/L, temperature: 80°C, dipping time: 10 min.

(4) Washing by tap water, room temperature, dipping for 30 sec.

(5) Soap treatment: Reactive soap lubricating matter on the market (PALUBE® 235, by Nihon Parkerizing Co., Ltd), concentration 70g/L, temperature: 80°C, dipping for 5 min

(6) Drying: 80°C, 3 min

(Comparative example 4)

Aqueous lubricant 8 as below was used in treating process A above.

Aqueous lubricant 8

water soluble inorganic salt: borax: 10% lubricative agent: calcium stearate: 10% oil constituent: palm oil: 0.5%
surfactant: polyoxyethylene alkyl alcohol: 1% others
: water

amount of produced film, g/m² : 10

(Comparative example 5)

Aqueous lubricant 9 as below (containing 1 wt % of nonionic surfactant for dispersion) was used in treating process A above
Aqueous lubricant 9
water soluble inorganic salt : sodium tetraborate
synthetic resin : urethane resin
metallic salt of fatty acid : calcium stearate ratio in
solid state (water soluble inorganic salt / synthetic resin) = 2/2
ratio in solid state (calcium stearate / synthetic resin) = 3/1
amount of produced film, g/m² : 10

Test results are shown in Table 1. It is clear from Table 1 that embodiment example 1-5 where aqueous lubricant for working of metallic material according to the present invention exhibit the excellent lubricity and simple and easy treating process.

Comparative example 1 where lubricative agent is not contained and comparative example 2 where wax is not contained are inferior in their lubricative properties. In comparative example 3, where treatment was carried out in a conventional process of using the chemical conversion layer of phosphate and reactive soap, the lubricative property is as excellent as in the present invention. However, much waste matter may appear from the reaction of chemical conversion, and special complicated equipments become necessary in disposal of waste water and for controlling the aqueous lubricant, and the burden for keeping the environment become increase.
Also it is proved that the lubricity in spike test are inferior in comparative example 4 which is the same as those shown in JP10-008085A and in comparative example 5 which uses synthetic resin as main constituent and is the same as those shown in JP2000-063880A.

ADVANTAGE OF THE INVENTION

As it is clear from the description of above, it became possible to produce the film with the high lubricity in the simple and easy treatment by using the aqueous lubricant and the method of lubricative film processing of the present invention. Also, the amount of arised waste matter was decreased and the preferable environmental protection became possible. Thus, this invention has a great industrial applicability.
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CLAIMS

1. An aqueous lubricant for plastic working of metallic material which comprises (A) a water soluble inorganic salt being selected from the group consisting of sulphate, silicate, borate, molybdate, tungstate, and combinations thereof, (B) at least one lubricative agent being selected from molybdenum disulfide and graphite, and (c) wax; and these components are dissolved in water in a weight ratio of (B) / (A) in solid state in the range of 1.0 to 5.0 and in a weight ratio of (C) / (A) in solid state in the range of 0.1 to 1.0, and which does not contain any other synthetic resin than the wax (C).

2. The aqueous lubricant for plastic working of metallic material according to claim 1 wherein the wax is water dispersed natural wax or synthetic wax having a melting point between 70 to 150 °C.

3. A method of lubricative film processing wherein an aqueous lubricant according to claims 1 or 2 is applied to a cleaned surface of a metallic material and is dried to produce the lubricative film of 0.5 to 40 g/m² on the surface of the metallic material.

4. The method of lubricative film processing according to claim 3 wherein the cleaned surface is obtained by one or more than one cleaning step being selected from the group consisting of shot blasting, sand blasting, alkali degreasing and acid cleaning.
5. The method of lubricative film processing according to claim 3 or 4 wherein the aqueous lubricant according to claim 1 or 2 is applied to the metallic material after the metallic material is heated to 60 to 100 °C.
(A) SAMPLE BEFORE REAR PUNCHING

(B) PUNCH

(C) SAMPLE AFTER REAR PUNCHING