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AN ADHESIVE SHEET FOR PREVENTION AGAINST
AQUATIC GROWTHS AND A METHOD FOR STICKING
THE ADHESIVE SHEET.

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The present invention relates to an adhesive sheet for prevention against aquatic growths such as animals and plants which will attach and propagate on the surface of ships and other structures in contact with water.

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Usually, on the surface of ships and other underwater structures, animals such as barnacles, mussels oysters and pearl-oysters, as well as plants such as various kinds of seaweeds will attach and propagate to produce a bad influence on navigation amongst others, so that various means are taken to prevent the adhesion and propagation of these animals and plants. For example, there is a method to apply paint containing a poisonous substance dissolving a very small amount thereof in sea-
10 water, however the paint must be recoated every 1 to 2 years to continue the effect of preventing the adhesion. Also, a method for preventing the adhesion of noxious animals and plants by using copper plate is known, however, since chemical reactions between copper and seawater will
15 proceed comparatively rapidly, there is a problem on durability unless fairly thick copper plate is used. Thus this method is not practical.

The inventors devoted themselves to study these
25 problems, wherein copper is alloyed to minimize the

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dissolving out of copper ions into seawater and with copper alloy plate to withstand the corrosion due to seawater for a long period, as well as to simplify the enforcement onto the underwater structures, thus to complete an adhesive sheet for prevention against aquatic growths with excellent durability.

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In the present invention, one surface of copper-nickel alloy plate with a weight ratio of copper to nickel of 100:0 to 80:20, is provided with a pre-determined pressure sensitive adhesive layer, existing on a primer layer, so that this sheet will prevent the adhesion and propagation of aquatic growth, and yet the dissolving out of copper ions into seawater is minimized as well as the enforcement being made easy and the sheet is durable for use over a long period of time.

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Fig. 1 is a perspective view showing a part of an adhesive sheet for prevention against aquatic growth according to the present invention.

Fig. 2 is a sectional view of Fig. 1.

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The adhesive sheet (6) for prevention against aquatic growths is based on copper nickel alloy plate as a base material (1), with a ratio of copper:nickel of 100:0 to 80:20 by weight; one surface of which is primer treated to form a primer layer (2), on which primer

layer a pressure sensitive adhesive layer (3) having waterproof and weatherproof properties is provided in a required thickness, and on which pressure sensitive adhesive layer, a release paper (4) is attached as the occasion demands.

If the thickness of copper-nickel alloy plate forming the base material is more than 0.05mm, the plate is stable in its strength and able to be used. The durable years of the plate are proportional to its thickness, for instance: the durable years of alloy plate of about 0.1mm thick, of which the copper:nickel ratio is 90:10, are about 5 to 10 years. In the case where the content of copper in the alloy is 100%, the melting speed of copper ions in seawater is large, and the effect of prevention against aquatic growth is excellent, however, the durable years thereof are comparatively shorter than those containing a predetermined quantity of nickel.

The primer layer contains as the main materials, elastomer, tackifier resin, epoxy resin and curing agent of epoxy resin, and as the occasion demands, anti-injurious agents of copper for a pressure sensitive adhesive and anti-aging agents are added, these components are mixed in their necessary quantities and melted into a mixture of a single or more than two kinds of organic solvents, such as toluene, ethyl acetate, methyl ethyl ketone, acetone and isopropanol to form an about 1 to 50% (weight %) solution, and are

12 painted on a necessary surface of base material so as to become a solid part of about 1 to 20 g/m², preferably about 3 to 10 g/m², thus the required primer layer is formed. As the elastomers, there are, for example, epoxy modified
5 natural rubber, (modified) methyl methacrylate grafted natural rubber, styrenebutadiene rubber, nitrile rubber, chlorinated rubber and their modified rubbers. And, as the tackifier resin, there are, for example, those named as tackifier resin in the pressure sensitive adhesive layer
10 component and phenol resin. And, as the epoxy resin, there are, for example, polyfunctional epoxy compounds such as ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, and as the curing agent for these epoxy resins, there
15 are polyamines such as diethylene triamine, triethylene tetramine, diethyl aminopropylamine, polyamides such as "Varsamid 110", "Varsamid 125", "Varsamid 140" sold by the General Mills Company, and "Lancast A" sold by the Ciba-Geigy Company, polycarboxylic anhydride such as phthalic
20 anhydride, dodecyl succinic anhydride, methylnadic anhydride, methyl tetrahydro phthalic anhydride, polysulfide, poly-mercaptan, dicyandiamine, resol type or novolak type phenol resin, and imidazole compounds such as 2-ethyl-4-methyl imidazole, 1-cyanoethyl-2-phenyl imidazole, and these
25 compounds are blended to a polyepoxy compound with an epoxy equivalent.

The blending ratio of the elastomer, tackifier

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resin and epoxy resin which are forming the primer layer is exemplified in that 100 weight parts of elastomer, 20 to 300 weight parts of tackifier resin and 30 to 200 weight parts of epoxy resin are blended, to which a curing agent corresponding to an epoxy equivalent is blended. For the antioxidant to be blended in the primer layer, the same substance blended to pressure sensitive adhesive may be used, and the blending quantity is about 0.5 to 5 weight parts to 100 weight parts of elastomer. And, as anti-injurious agents of copper, there are, for example, N-isopropyl -N'-phenyl-P-phenylene diamine, N, N'-diphenyl-P-phenylene diamine, N,N'-di-2-naphthyl-P-phenylene diamine, and their blending quantity is about 0.1 to 3 weight parts to 100 weight parts of elastomer.

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The pressure sensitive adhesive layer is formed of elastomer, tackifier resin, vulcanizing agent, antioxidant as the main materials, and the thickness of the layer is about 20 to 1000 μ , preferably about 100 to 400 μ . The formation of a pressure sensitive adhesive layer is more preferably a solventless system, because, by means of a solvent system, residual solvent which requires much time for drying, may exert a bad influence upon the durability.

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The pressure sensitive adhesive layer is particularly preferably a cross linking type to obtain durability for a long time. As the elastomer component forming the pressure sensitive adhesive layer, there are those having weatherability and waterproof properties,

such as natural rubber, modified methyl methacrylate grafted natural rubber, polyisobutylene rubber, butyl rubber, styrene-butadiene rubber, styrene-isoprene-styrene block copolymer rubber, styrene-ethylene-butylene-styrene block copolymer rubber, reclaimed natural rubber and re-

5 reclaimed butyl rubber.

As the tackifier resin, there are polyterpene resin, terpene phenol resin, resins of the rosin group,

10 resins of the rosin ester group and their hydrogenated resins, and petroleum resins such as C5 series petroleum resins, C₅ to C₉ copolymerised series resins, C₉ series petroleum resins and their hydrogenated resins, and in case the property of long period weatherability is

15 needed, hydrogenated resins are particularly preferable.

As the vulcanizing agent and auxiliary agent of vulcanization which are added for making the pressure sensitive adhesive into a cross linking structure, there

20 are a resin type such as reactive phenol resin and a sulphur type. To the pressure sensitive adhesive, fillers such as clay, zinc white, calcium carbonate, magnesium carbonate, carbon black, silicate are added to promote the vulcanizing effect and as well weighting and re-

25 inforcement effects may be achieved. As an antioxidant, those with amine groups, alkyl phenol groups, thiourea groups or benzimidazol groups may be suitably used.

The pressure sensitive adhesive sheet of the

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present invention, which is formed as above mentioned,
is for instance, when this sheet is stuck on the hull
of a fibre reinforced plastic vessel such as a yacht, the
portion of the hull where the sheet is to be stuck, is
5 preliminarily cleaned in a suitable manner to fully remove
contamination which is harmful for the adhesion of adhesive
so as to cause no clearance between the pressure sensitive
adhesive sheets, thus to strongly press the sheets to be
closely contacted without having a bubble between the
10 sticking surface of the hull and the adhesive sheet. In
this case, if the sticking surface of the pressure
sensitive adhesive sheet is preliminarily primer processed,
much stronger adhesion may be effected. This primer
layer is effected by using a primer solution applied to
15 the surface of the base material and is similarly processed
to form the necessary primer layer.

Some preferred embodiments will be given in the
following.

20 Example 1.

Raw material having the following blending ratio was
put into an enameled container and mixed by stirring for
about 5 hours to obtain a primer solution.

25	Heveaplus	Mg - 30*1	100 g
	Arkon	P - 100*2	100 "
	Epicoate	828*3	125 "
	Epicure	DX103*4	75 "
	Sumilizer	MDF*5	1 "
	Nocrac white	*6	0.5 "

Toluene 450 "

Methyl ethyl ketone 450 "

*1 - Trade Mark of natural rubber grafted
with 30% methyl methacrylate made by
ITO SHOJI COMPANY LIMITED.

*2 - Trade Mark of a hydrogenated petroleum
resin (softening point 100°C) made by
ARAKAWA CHEMICAL INDUSTRIES, LIMITED.

*3 - Trade Mark of a polyepoxy compound made
by UKA SHELL EPOXY K.K.

*4 - Trade Mark of a curing agent of epoxy
resin made by Uka Shell Epoxy Kabushiki Kaisha

*5 - Trade Mark of a bisphenol group anti-
oxidant made by Sumitomo Chemical Company
Limited.

*6 - Trade Mark of an amine group anti-
oxidant made by OUCHI-SHINKO CHEMICAL
INDUSTRY CO. LTD.

The above mentioned primer solution was applied on one
surface of a copper-nickel alloy plate with a copper-
nickel weight of ratio of 90:10, having width 400mm x length
10m x thickness 0.1mm, then a pressure sensitive adhesive
layer of the following composition was applied on the primer

layer by a calender roll so that its thickness became 150 (microns), a release paper was stuck on the pressure sensitive adhesive layer, and the thus obtained adhesive sheet was coiled round on a paper tube of about 7.6cm (3 inch) bore to obtain a pressure sensitive adhesive sheet for prevention against aquatic growths according to the present invention. 180° peel adhesion to a fibre reinforced plastic plate (FRP) of 3mm thickness of the obtained adhesive sheet was 2.6 kg/25mm (measuring temperature 23°C, 65% relative humidity), the primer solution was applied on a FRP plate of 3mm thickness so that the painted amount after drying became 4 to 6 g/m², and 180° peel adhesion of the adhesive sheet to this primer layer forming surface was 7.5 kg/25mm, and due to the formation of the primer layer, the adhesion and the durability between the alloy plate base material and the adhesive agent is stabilized and as well the adhesion between the adherent and adhesive agent can be remarkably improved.

20 Blending of adhesive agent:

Natural rubber (smoke coat)	100	parts (weight)
Calcium carbonate	70	"
Zinc white	30	"
Carbon black	3	"
25 Super ester L *7	30	"
Process oil	10	"

Arkon P - 100 *2	100	"
Alkyl phenol disulfide	5	"
Dibutylditho zinc carbamate	1	"
Sumilizer MDP *5	3	"

5 *7 - Commodity name of a liquid rosinester resin made by ARAKAWA CHEMICAL INDUSTRIES, LIMITED.

*2, *5 - cf. above mentioned primer blending

After the primer liquid was applied so that on both of the inside and outside surfaces of FRP plate of length
10 300mm x width 210mm x thickness 3mm, the applying amount after drying becomes 4 to 6 g/m², the adhesive sheet of the present invention was stuck on the primer layer of both inside and outside surfaces, the plate was suspended at
15 1m under the water level of seawater introduced in the laboratory of our company for one year and the condition of adhesion of aquatic growths was observed. As a result, after the lapse of one year, there was no adhesion of any aquatic growth and no peeling from the adherent surface of the adhesive sheet.

20 Further, the primer liquid of the blending was applied on an FRP plate of 50 mm length x 125 mm width x 3 mm thickness so that after drying, its application amount would become 4 to 6 g/m² and after drying, 20 samples were prepared, on which test pieces of the adhesive sheet
25 of the present invention of 25mm width were stuck, and these samples were immersed in salt water of 3.5% concentration held at the temperature of 40°C, and the change was investigated with the lapse of time. As a result, 180°

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peel adhesion after one month was 7.6 kg/25mm and there was almost no change.

Comparative example 1:

FRP plate of length 300mm
5 x width 210mm x thickness 3mm was suspended at 1m under the water level of seawater for one year in the same way as Example 1, and the condition of adhesion of aquatic growths was observed, resulting in that after one year, remarkable adhesion of barnacles and seaweed was found.

10 Example 2:

Similar to Example 1, a primer liquid was applied on the surface of a copper plate of 400mm width x 10m length x 0.1mm thickness to form a similar primer layer, on which a similar pressure sensitive adhesive
15 layer is provided, to which layer a release paper was stuck to obtain an adhesive sheet for prevention against aquatic growths according to the present invention. Similar to Example 1, as to the obtained adhesive sheet, its peel adhesion, and condition of adhesion of aquatic growths were
20 tested, of which the results were as follows. Utterly no adhesion of aquatic growths due to leaving the adhesion sheet in seawater for one year was found. 180° peel adhesion to the FRP plate was 2.4 kg/25mm and 180° peel adhesion to the primer processed FRP plate was 7.6 kg/25mm, immersed in
25 salt water of 3.5% concentration at 40°C temperature, and 180° peel adhesion after one month was 7.4 kg/25mm, showing almost no change.

Comparative example 2:

An adhesive sheet was made similar to those described in Example 1, except the primer processing on the surface of the base material of copper-nickel alloy plate. The thus
5 obtained adhesive sheet to which primer was not applied, was stuck on both the surface and back sides of the FRP plate of length 300mm x width 210mm x thickness 3mm, the plate was suspended at 1m under the water level of seawater introduced in the laboratory of our company for one year
10 like Example 1. The result was that on the surface side of FRP plate, the adhesive sheet was stuck hard and on this surface aquatic growths were not found, however, on the back side of the FRP, the adhesive sheet had peeled off and on the surface of FRP, barnacles and seaweeds were attached.
15 And, 180° peel adhesion to FRP plate of adhesive sheet to which a primer was not applied, after one month immersion in seawater of 3.5% concentration at 40°C temperature was in any case remarkably inferior relative to Example 1 and 2.

As mentioned above, the adhesive sheet for
20 prevention against aquatic growths according to the present invention is excellent in the effect of prevention against adhesion of aquatic growths and almost no degradation of adhesion during lapse of along time in seawater, achieving adhesion performance with excellent durability.

25 The present invention has the above mentioned formation, and may be easily stuck on a surface in contact

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with water of steel plate ships, wooden ships, reinforced plastic ships, ferrocement ships and other ships and yet no degradation due to oxidation of pressure sensitive adhesive copper or copper alloy plate .

- 5 may be safely and surely held on the outside surface of the hull without falling off, and sticking and propagation of mussels, barnacles, seaweeds and other growths may be prevented and as well the corrosion of the hull of, for example, steel plate and other structures under water may be
- 10 prevented. This adhesive sheet has an excellent effect when applied to other than ships, for instance, steel piles used for quay walls, other iron materials, inside faces of seawater conduits for cooling in power plants, outside faces of these conduits always in contact with
- 15 seawater, structures of seawater intake gates, for the purpose of preventing against adhesion of aquatic growths and corrosion.

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What is claimed is:

1. An adhesive sheet for application to a construction
5 for preventing the fouling of the construction's
underwater surface by aquatic growths comprising:

a copper of a copper-nickel alloy plate having a
weight ratio of copper:nickel in the range of 100:0 to
80:20;

- 10 a primer layer formed on a surface of the plate;
and

a pressure-sensitive adhesive layer formed on the
primer layer;

- wherein the primer layer comprises elastomer,
15 tackifier resin, epoxy resin and epoxy resin curing
agent,

- wherein the primer layer includes at least one
elastomer selected from the group consisting of
modified natural rubber, styrene-butadien rubber,
20 nitrile rubber and chlorinated rubber, and

wherein the primer layer comprises 100 parts by
weight of elastomer, 20-300 parts by weight of
tackifier resin, 30-200 parts by weight of epoxy resin
and an epoxy equivalent curing agent.

- 25 2. An adhesive sheet for prevention against aquatic
growths according to claim 1, wherein the pressure
sensitive adhesive layer contains natural rubber or
synthetic rubber as elastomer, with which tackifier
resin, filler, cross linking agent, auxiliary agent of



cross linking and antioxidant are blended to form an adhesive of excellent antiaging property.

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3. An adhesive sheet for prevention against aquatic
5 growths according to claim 1 or 2, wherein said primer
layer contains an anti-injurious agent of copper.

4. A method of sticking an adhesive sheet for
prevention against aquatic growths, characterized in
that when an adhesive sheet for prevention against
10 aquatic growths, in which a primer layer is provided on
the surface of copper-nickel alloy plate, on which a
pressure sensitive adhesive layer is formed, is stuck
on the surface of the object on which aquatic growth is
to be prevented, a primer layer of the same composition
15 as said primer layer is provided on the surface of said
object, on which said adhesive sheet is applied.

