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FLAME-SPRAYED COPPER ALLOY COATING FOR UNDERWATER SERVICE: CORROSION CONSIDERATIONS

By

Louis M. Riccio
President
Copperlok, Inc.

ABSTRACT

The Copperlok Coating is a new method of applying copper and copper/nickel to a hulls surface for anti-fouling purposes. The process involves the thermal spraying of a copper nickel alloy onto a specially modified epoxy resin base coat. The alloy in wire form is melted by an oxyacetylene flame, atomized by compressed air and the molten particles are propelled to the surface where they form a strong mechanical bond.

The coating can be built UD to Practical thicknesses of 10 to 12 mils which data shows should last 15 to 20 years on ships where hull speed is in the range of 8 to 12 knots.

Other applications such as off shore structures, power plants and heat transfer surfaces will be presented with slides. -The process and economic factors will be discussed. Samples of the coating will be available for inspection.

COPPERLOK™ LONG TERM ANTIFOULING COATINGS

LOUIS M. RICCIO, PRESIDENT

SEPTEMBER 11, 1985

Hull Biofouling has been a challenge to mariners throughout the history of commercial transport. Early Mediterranean traders covered their hull bottoms with lead sheathing to ward off hard fouling and wood borers.

The British Admiralty in the early 1700's used copper sheathing for the same purpose.

The China Clippers with precious tea cargoes and the clippers running between Australia and Britain with cargoes of wool knew the value of operating with a clean, non-fouling bottom. Using copper and various alloys like Muntz metal which was used on the Cutty-Sark, Fig. 1, consistantly helped this ship to break running records between these trade routes.

The New England Whalers of which samples can be seen today at Mystic Seaport, still wear their copper sheathing. In 1893 the America's Cup defender, Vigilant; used copper alloys and later in 1930 the Enterprise also utilized the benefits of copper alloys. Fig. 2, Fig. 3, Fig. 4. With the coming of steel hulls, copper sheathing gave way to copper based paints. The copper alloy development then centered on alloys with nickel content which offered the best strength and good corrosion resistance. 90-10 copper nickel (CA-706) and 70-30 copper nickel (CA-715) were used in vessels with good success.

With the backing of Copper Development Association and the International Nickel Company, some of the most thorough research to date is "the Copper Mariner's Experience and Economics" report presented in November 1976 SNAME meeting.
A note of particular importance is that the Copper Mariner average corrosion rate of copper nickel over a period of 52 months is less than .05 mils per year [1]. Cladding, sheathing and sheet copper with adhesives are all currently being used with varying successes to reach the main goal: To maximize the anti-fouling properties for longer periods than available now in anti-fouling painted surfaces.

Meeting this goal will benefit the Maritime Industry by lowering maintenance costs and lowering fuel costs. Fuel costs are recognized to account for no less than 50% of the total costs for operating a ship. Marine fouling of a ship's hull can significantly increase fuel consumption. Anti-fouling paints control fouling, but in general their effectiveness decreases with time and re-painting becomes necessary, introducing another cost factor. These factors produce an incentive for the improvement of present anti-fouling paints and for the development of new and innovative coating systems.

Because the previously mentioned methods of applying copper and copper nickel to hulls depend on welding, fitting and tailoring compounds shapes, the idea of using the technique of flame spraying the copper and copper nickel seemed to be a logical solution and this is the patented process employed by the Copperlok coating system.-

This process takes metal in the form of wire or powder, melts it by means of a combustion flame, such as oxygen and acetylene or electric arc, and propels it to the substrate in an atomized condition, by means of compressed air or the velocity of expanding gases as in the case of plasma-type equipment. Of the various thermal spray processes evaluation, the combustion process, with the use of wire, was determined to be the best starting point. Other variations fell short because of cost, excessive heat, complexity, weight and cumbersome aspects of the equipment. Some techniques are being developed further and may, for certain applications, supplant the combustion wire method.

Heretofore, the state-of-art of depositing a metallic coating on a plastic surface consisted of some sort of abrasion, such as a grit-blasting, followed by a coat of an easily deposited coating such as zinc or aluminium. If another higher melting coat was to be deposited, it would be sprayed over the aluminium or zinc or a nickel aluminide coating. The dissimilar metal combinations precluded this technique for marine use. Spraying copper directly on to grit-blasted gel coats can be achieved, but with very poor bond strengths. To build up any practical thickness of 10 to 12 mils would cause a delamination due to the residual stresses of the metal shrinkage overcoming the bond strength. The development of a modified resin coating which provided excellent strength to permit adequate build-up of the flame spray copper nickel coating was achieved after experimenting with various resins and fillers in the form of hollow micron sized silica spheres. Fig. 5. The aspects of water vapor transmission, high temperature excursions, adhesive properties, along with other constituents to improve wettability, leveling, thixotropic and other properties were part of the epoxy formulation.

Test panels were introduced at the Ocean City Research New Jersey facility'. Emersion tests were necessary to determine if the nature of the oxides might change using flame spray methods and to verify that the anti-fouling properties would remain. No fouling has occurred after the three-year period. Fig. 6, Fig. 7.

Six fiberglass pleasure boats use this Copperlok system to date and two wodden hulls, one of which is an entrant to the B.O.C., 1986/87 single-handed, around-the-world race. Fig.8.

The Copperlok process can be used in G.R.P. new boat construction by applying our bond coat epoxy in the mold first and masking at the water line afterwhich the use of standard laminates completes the hull ,layup. Fig. 9.

After curing and removal of the hull from the mold, the copper nickel thermal spray can be applied below the water line onto the bond coat.

Then applying Copperlok on steel surfaces, the epoxy bond coat with the anti-corrosion coatings, acts as a dielectric barrier and serves to insulate the copper nickel coating from the steel. Fig. 10. In tests at Ocean City Research, it was found that the copper nickel coating had no significant effect on the rate at which the underlying steel corroded at intentional coating holidays when there was no metallic electrical connection between the copper nickel and the steel. When there was an electrical connection between the copper nickel coating and steel, the steel corroded at the expected rapid rate.[2] A simple alarm system was developed to warn if a short occurs during application of Copperlok. In this system a simple continuity circuit is used to insure that the coating is not shorted to the steel. An alarm sounds to enable the repair or rework of the contact area.

The Copperlok application to the Exxon "Spinel" offshore structure in the Gulf of Mexico demonstrates the typical procedural steps. The coating of a casing pipe is treated as follows: The casing pipe is grit blasted; coated with a moisture barrier epoxy; Copperlok bond coat is applied; after curing, the bond coat is abraded and washed. Copper nickel is then flame sprayed to the desired thickness. Fig. 11, Fig. 12.

The use of current automation techniques will enhance the productivity of applying Copperlok onto piping. Fig. 13. The advantage of Copperlok to coat nodes of offshore structures can readily be seen since the process can be sprayed onto varied contours and shapes. Fig. 14, Fig. 15.

There is a need for anti-fouling coatings in power plant utilities using coastal waters. Coating concrete intake basin walls, concrete pipe, and steel pipe will aid to keep bio-fouling from entering and clogging the condenser tubes. Currently used methods introduce chlorides and bromides into the intake water to keep bio-fouling under control, but chlorine and bromide effluent levels must be monitored closely.

Copperlok coatings can be applied to a variety of substrates and offers to reduce or eliminate the use of bromides.

The Copperlok system lends itself to automation and to the advances in robotic adaptive controls. I believe large hull surface coatings are feasible with relatively short development time. Fig. .16. If our industry is to be competitive in world marine markets, we should readily see the economic benefits to a fifteen year anti-fouling coating.

1) J. L. Manzolillo, E.W. Thiele, A.H. Tuthill, CA-706
Copper-Nickel Alloy Hulls: The Copper Mariner's
Experience and Economics

2) Dynamic Corrosion Testing "COPPERLOK" Coating System,
National Shipbuilding Research Program
U.S. Dept. of Transportation
Maritime Administration in cooperation with
Avondale Shipyards

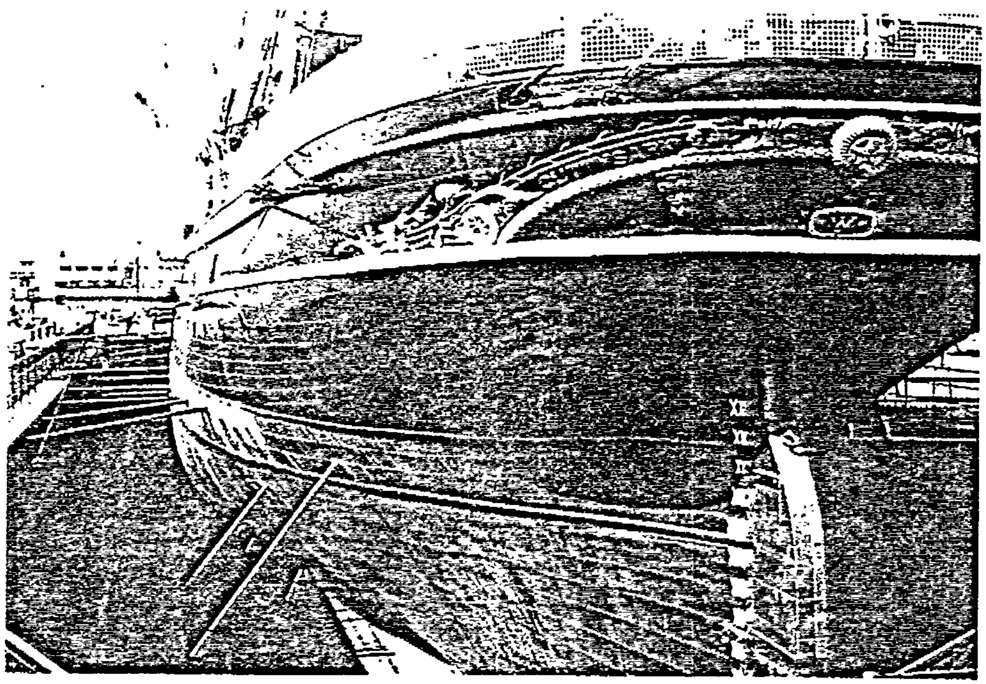


FIG. 1

FOULING RESISTANT PROPERTIES

Initial Corrosion of 90/10 Cu:Ni Produces a Stable and Protective Cuprous Oxide Corrosion Product Film. Complexing with Chloride Ions from the Sea Water Results in Gradual Formation of a Surface Layer of Cuprous Hydroxychloride. This Salt has Limited Solubility, But it is Sufficient To Inhibit the Attachment of Free Swimming Larvae on the Exposed Metal Surfaces.

Source: INTERNATIONAL NICKEL COMPANY, INC.
Corrosion Resistance of Wrought 90/10 Copper-Nickel-Iron Alloy in Marine Environments

FIG. 2

FOULING RESISTANCE — QUIET SEAWATER

Above 3 ft. per sec. continuous velocity—about 1.8 knots—fouling organisms have increasing difficulty in attaching themselves and clinging to the surface, unless already attached securely.

Arbitrary Rating Scale of Fouling Resistance		MATERIALS
90-100	Best	Copper 90/10 copper-nickel alloy
70-90	Good	Brass and bronze
50	Fair	70/30 copper-nickel alloy, aluminum bronzes, zinc
10	Very Slight	Nickel-copper alloy 400
0	Least	Carbon and low alloy steels, stainless steels, nickel-chromium-high molybdenum alloys Titanium

Source: INTERNATIONAL NICKEL Guidelines for Selection of Marine Materials

FIG. 3

MARINE CORROSION CHARACTERISTICS OF WROUGHT 90/10 Cu:Ni

Corrosion Attack Is Minimal, Progressing at a Uniform Rate of .03-.05 Mils Per Year with No Significant Pitting.

Source: INTERNATIONAL NICKEL COMPANY, INC.
Corrosion Resistance of Wrought 90/10 Copper-Nickel-Iron Alloy in Marine Environments

FIG. 4

COPPER-NICKEL

HOLLOW MICRON SIZE

Silcon spheres

EPOXY

COPPERLOK COATING SYSTEM

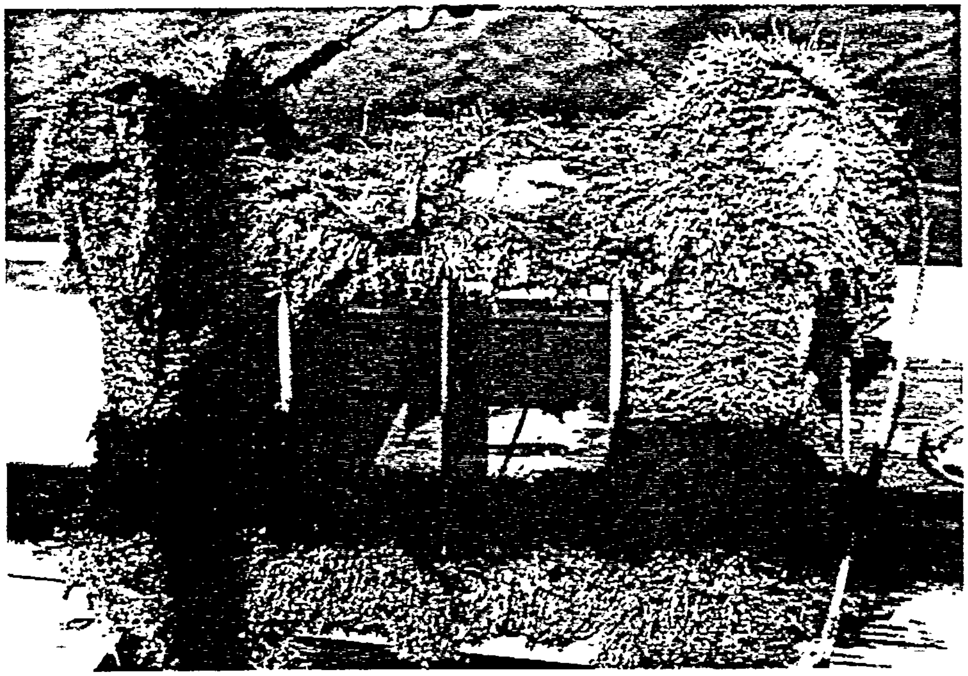


FIG. 6

30 DAY
EMERSION

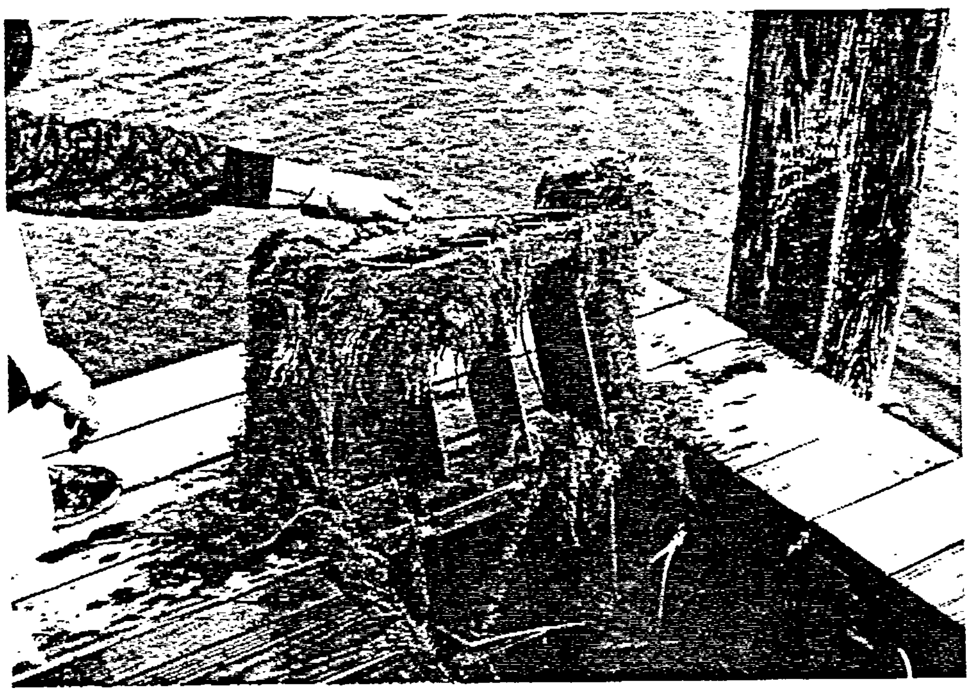
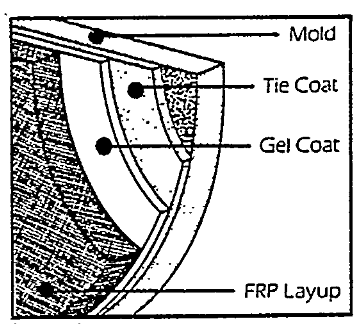


FIG. 7

90 DAY
EMERSION

FIG. 8



In mold application

FIG 9.

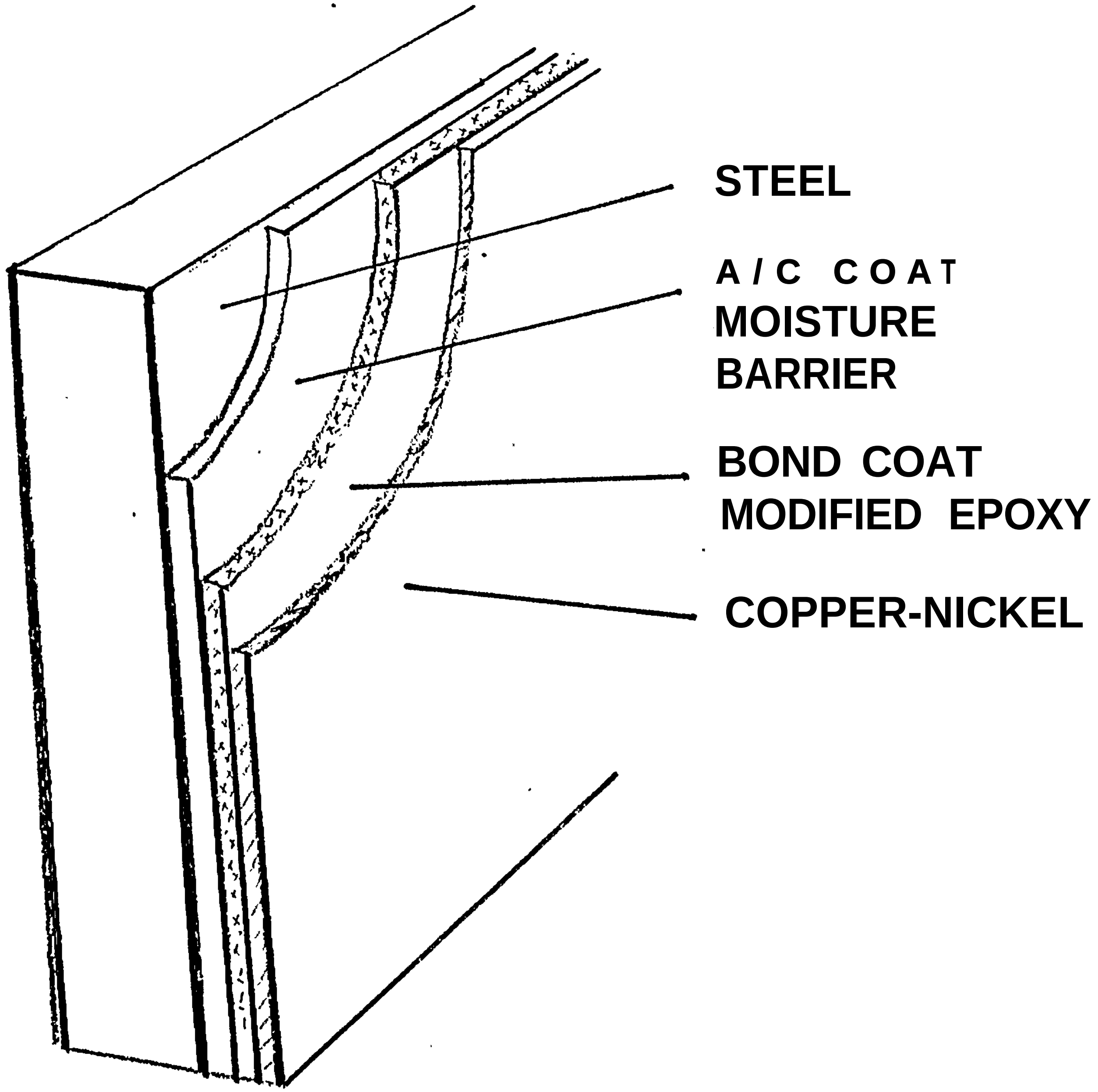


FIG 10

TYPICAL COPPERLOK APPLICATION

FIG. 11

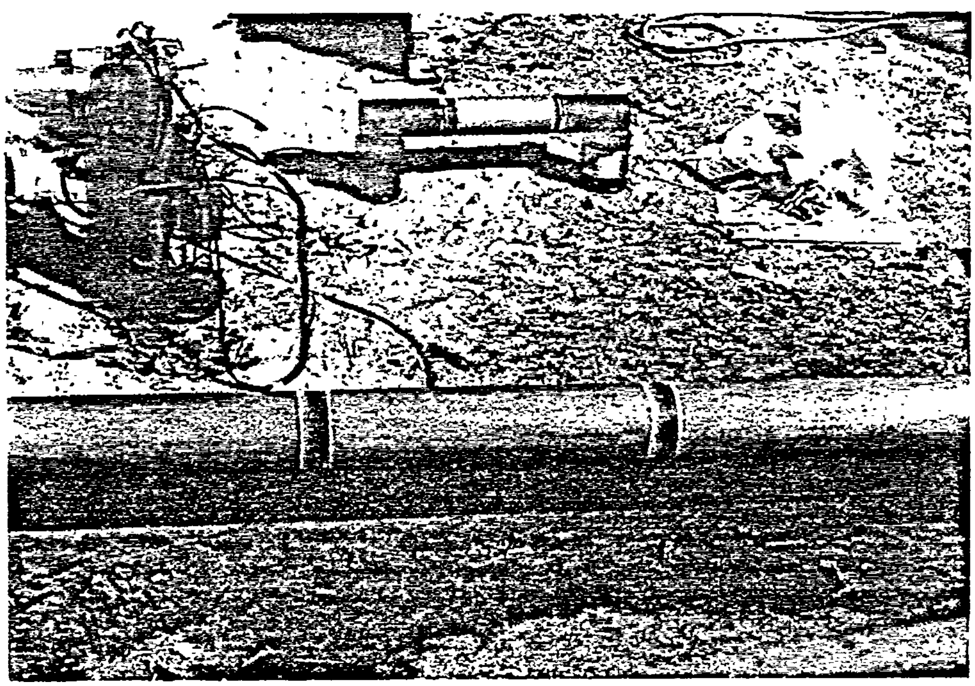


FIG. 12

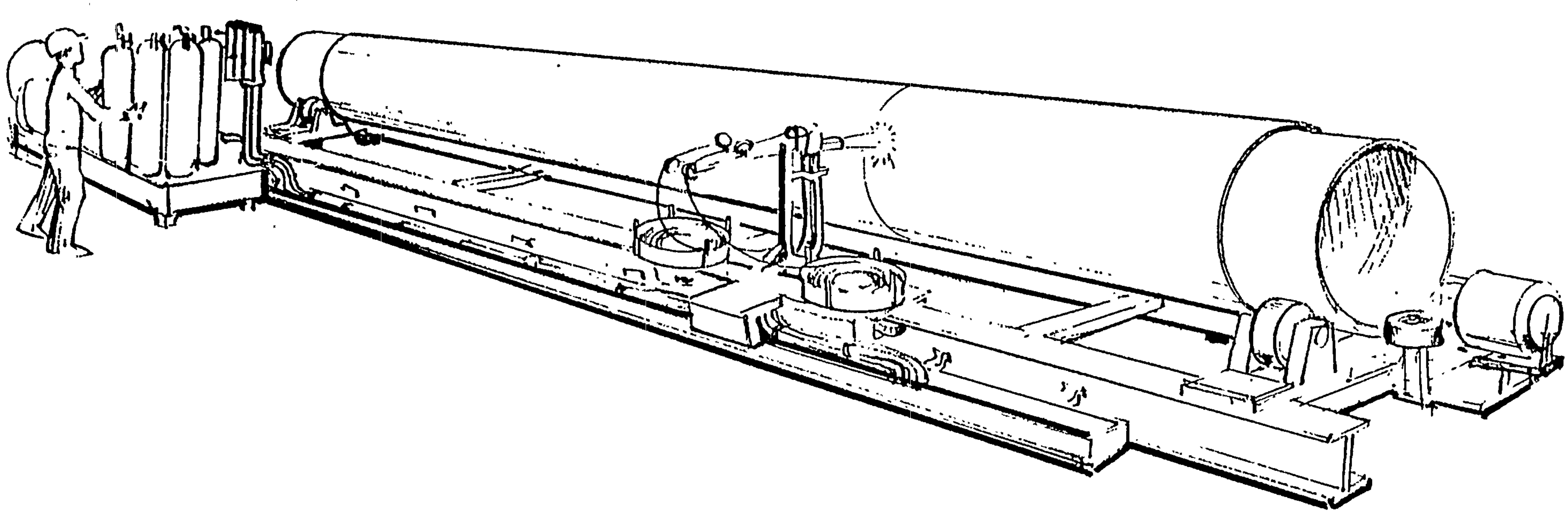


FIG 13

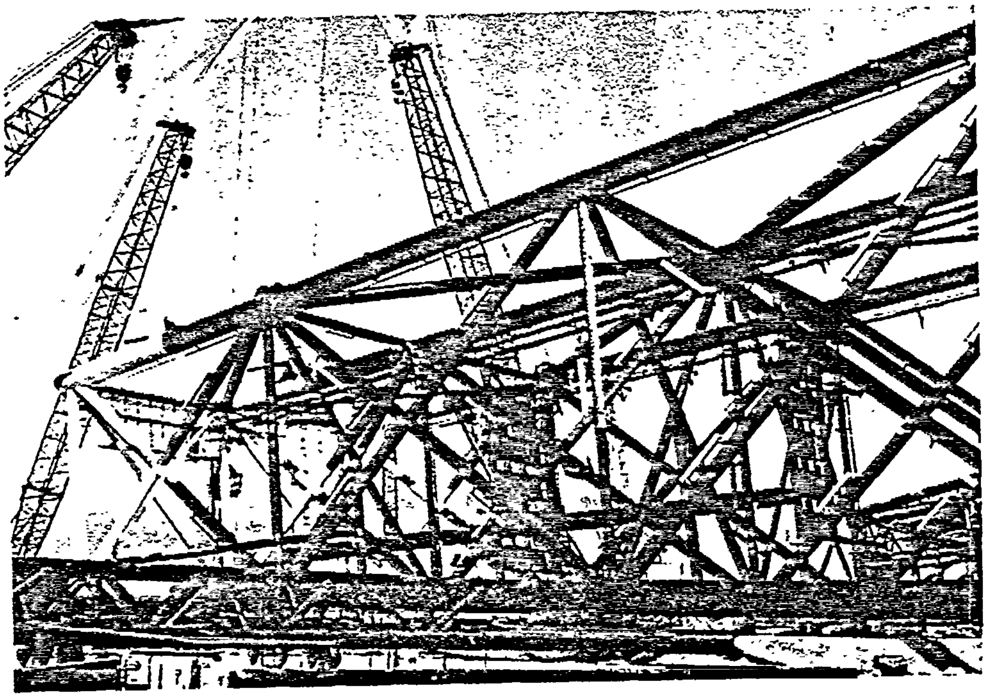


FIG. 14

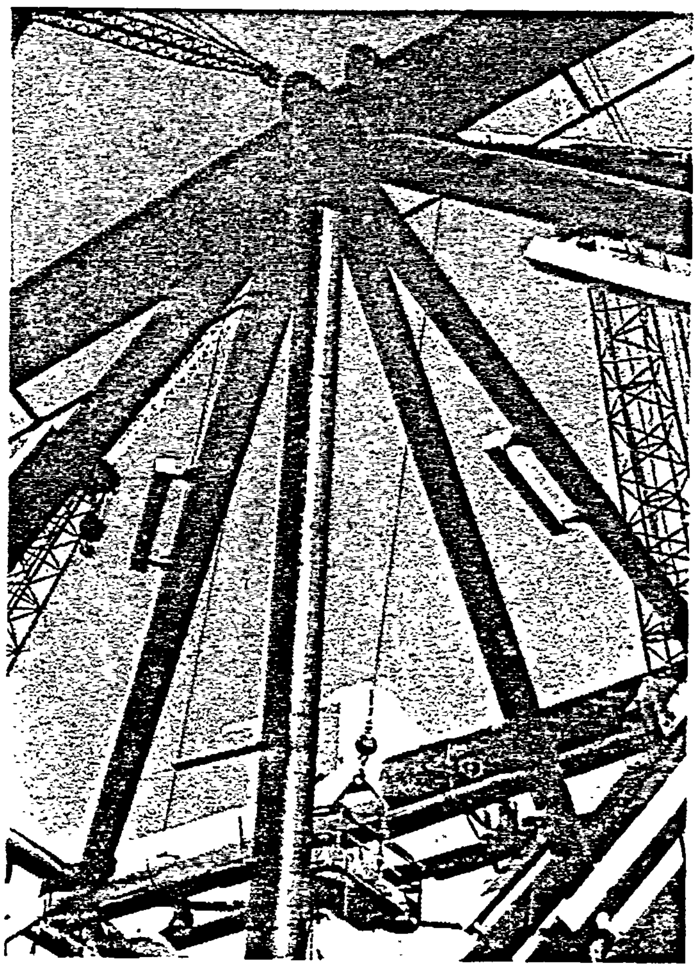


FIG. 15

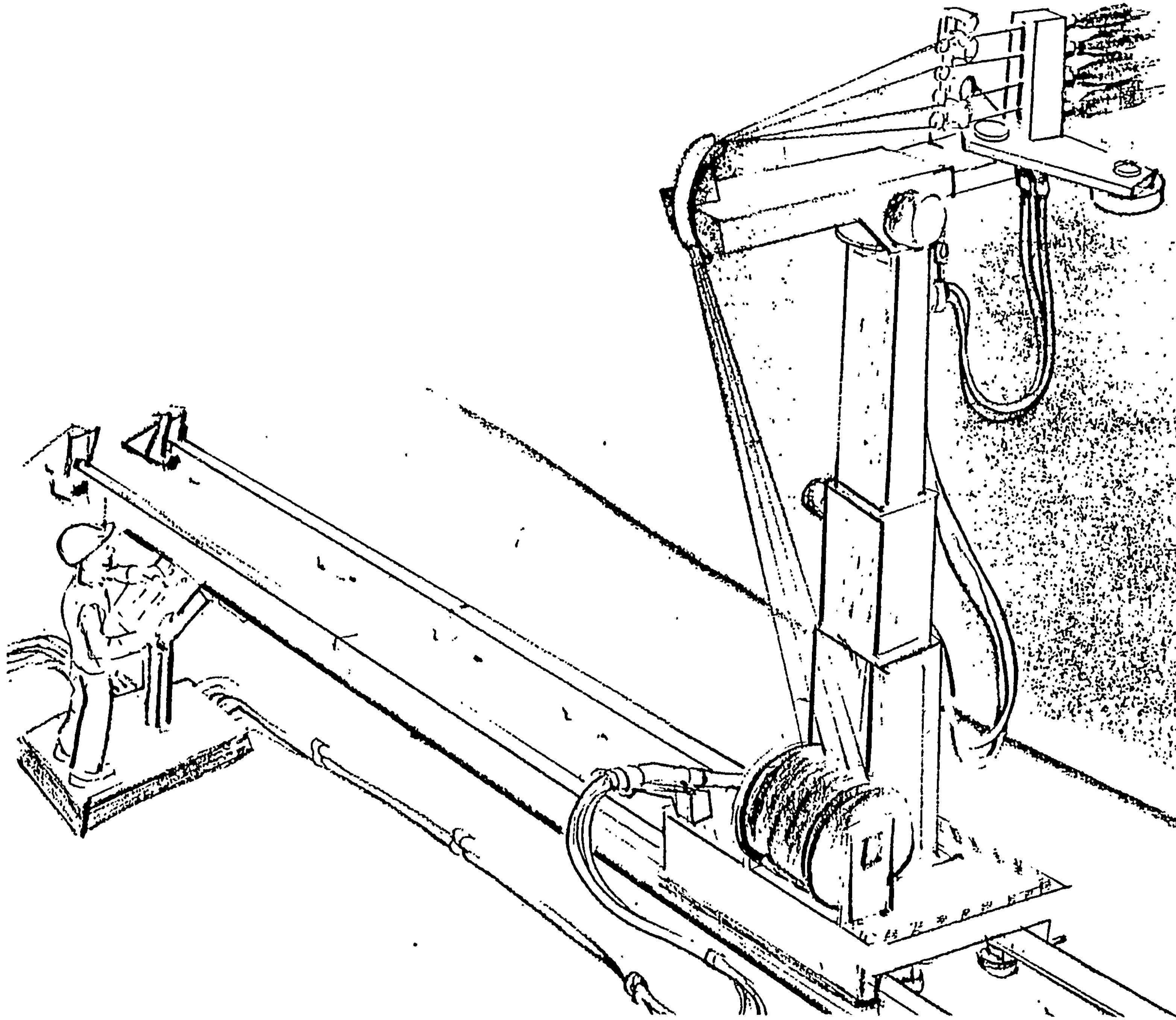


FIG. 12

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