# Clear Organic Finishes for Copper and Copper Alloys

The distinctive colors of copper and copper alloys make them prized for architectural and consumer items and objects of art. Their natural metallic tones range from reddish to silvery and a number of other colors can be obtained by chemical or electrochemical processing. Copper and its alloys are extremely resistant to corrosion, but a superficial discoloring tarnish eventually forms with exposure to the atmosphere or handing. The appearance of these metals can be preserved by applying thin clean protective coating to their surfaces. These coatings are organic chemicals which harden at room temperature or with baking and are usually applied in a solvent vehicle.

There are hundreds of useful clear coating products on the market, formulated from numerous polymers, solvents, and additives. The user selects from these coating based upon economics, intended life, desired transparency, and the expected service conditions.

Many coating manufactures prefer to custom blend coatings and work closely with the user to solve his particular problems. There are also a large number or standard compositions which can be ordered by trade name and which will satisfy many needs.

Because of the wide range of compositions available only general characteristics of the various systems and additives are reviewed here. Test results for representative coating systems are presented to indicate the range and type of properties which may be obtained. But it must be remembered that the effectiveness of a finish also depends on the composition of the underlying metal and on the cleaning and application procedures used when coating.

It is not possible to quantitatively predict from its properties how long or how well a coating will protect the substrate. To answer this question it is necessary to apply the coating to the mental under shop conditions and expose the combination to an environment representative of the intended service.

## Serviceability

Coatings are available which can protect copper-base metals for many years under ideal conditions. However, handling, humidity, air pollution, sunlight, and abrasion all work to reduce the life of a coating. For example, coating life is usually short in exterior application in cities with severe air pollution.

In selecting a coating it must be realized that maximizing resistance to one type of service condition may reduce resistance to others. Also, if the life of the article is expected to be longer than any reasonably attainable coating life, a coating that can be stripped off with a solvent must be selected so that the article may be restored when the coating and appearance have degraded to an unacceptable level.

Some examples of coating performance indicate the range of serviceability of organic finishes on copper and its alloys.

An air-drying acrylic lacquer with a tarnish inhibitor (benzotriazole*) has protected a bronze nameplate outdoors in urban New Jersey for more than five years. The same coating indoors on handrails and other objects subjected to wear failed in less than one year.

A combination of a silicone primer and an acrylic top coat displayed excellent appearance after more than six years or service in interior applications with moderate or no abrasion. The same system darkened significantly in one year of open exterior exposure but indicated good performance for more than three years on sheltered doors of office buildings and churches.

A nitrocellulose lacquer failed in less than one year of open exterior exposure. Urethane lacquers lasted about one year under the same conditions.

Baked alkyd-butyl and butyl coatings looked good after two years of open exterior exposure. Epoxy coatings darkened in four to six months.

Silicone thermoset coatings retained good protection qualities after 62 days at 200 F or 100 hours at 300 F.

Antiqued brass automotive interior trim has been protected with a thermosetting epoxy clear coating.

The copper roof of the Sports Palace in Mexico City is covered with an air drying acrylic lacquer formulated with an inhibitor and organic ultraviolet absorbers.

Bathroom fixtures of brass have been satisfactorily protected for more than five years with a baked epoxy coating.

*Benzotriazole: An Effective Corrosion Inhibitor for Copper Alloys. Application Data Sheet 108/9, Copper Development Association Inc., New York (1969)

## Basic Coating Systems

***Nitrocellulose.*** Nitrocellulose coatings are the least expensive and most common air drying coatings for interior service. They are modified with alkyd or acrylic resins. Nitrocellulose coatings are used in exterior applications; however, they are usually stripped and replaced at intervals of less than one year. They do not have high resistance to chemicals, but they are fast drying and easy to use.

***Acrylic.*** Available in air drying or thermosetting compositions, acrylics are relatively high cost materials. The air drying modifications are popular for exterior applications, while the thermosetting types are useful for interior applications requiring high resistance to heat and abrasion. Since the thermosetting coatings are not conveniently stripped, they are unsuitable for major architectural applications.

***Epoxy Coatings.*** Epoxy coatings have excellent resistance to wear and chemicals. They are relatively expensive and are only available in thermosetting or two part (catalyst activated) compositions with relatively short pot lives. They are good for severe indoor applications, but they degrade rapidly and darken in a few months of exterior service.

***Silicone Coating.*** Silicones provide the best potential for coatings which must operate at elevated temperatures. Thin films of these high-cost coatings are used and protection by a second coat of a more durable abrasion resistant lacquer may be necessary. Ultraviolet absorbing compounds are added to prevent darkening of the silicone during exterior exposures.

***Alkyd Coatings.*** Slow drying or baking is required when applying the alkyd coatings. Modified with melamine resins, these coatings are low cost and durable enough for exterior applications. Resistance to chemicals is usually good.

***Urethane Coating.*** Color degradation on exterior exposure has been a problem with urethane coatings. Resistance to chemicals and abrasion are good even for the air drying coatings.

***Cellulose Acetate Butyrate.*** Usually considered for interior applications, cellulose acetate butyrate coatings are air drying and have moderate cost and properties. They have a tendency to darken during exterior applications.

***Vinyl.*** Vinyl coatings require stabilization against ultraviolet degradation. They are usually relatively soft and flexible coatings.

***Polyvinyl Fluoride Film (Tedlar®).*** Applied by roll bonding with an adhesive, Tedlar films have been used to protect sheet copper in exterior applications. It has been projected that these clear films can protect a properly prepared substrate for twenty years or more.

Tedlar®-Registered trademark of Du Pont Co.

## Additives

Among the common coating additives are the following types:

***Ultraviolet Absorbers.*** Ultraviolet absorbers are organic compounds which are sometimes added to coatings for exterior applications in order to prevent darkening and degradation of the coating. In some cases they may also interact with the substrate and prevent tarnishing.

***Leveling Agents.*** Leveling agents improve the flow properties of coating and thereby provide better surface appearance. In addition, the likelihood of pin holing or other defects is reduced.

***Chelating Agents.*** Benzotriazole and other chelating agents interact with copper and its alloys to prevent tarnishing. Chelating agents are preferentially absorbed on the surfaces of the metals and act as an invisible barrier to elements or compounds whish might cause corrosion. In this way they protect the metal against oxidants permeating through the coating and continue to protect even after a minor defect has formed in the coating. Chelating agents may be included in the coating formulation or applied as part of a pretreatment procedure.

***Antioxidants.*** Antioxidants reduce the degradation of coatings during long and severe exposure. Examples are hydroquinone, N-propyl gallate, and modified phenol and cresol compounds.

## Application

No coating can perform to expectations if applied to a poorly prepared surface. The metal surface must be free of contaminants such as dirt, oil, dust, old finishes, and finger prints. Coating should be done with a minimum of delay after cleaning and precautions should be taken to prevent recontamination. Precautions include working in a low dust environment, handling with white gloves, and applying tarnish inhibitors (chelating agents) to the surface.

Ordinary steel wool should not be used in cleaning as the pads may contain chemicals which stain copper metals. Suitable abrasives are silicon carbide (Scotch-brite) pads or wheels, stainless steel pads, and powdered pumice stone. The pumice powder is slurried in a 5% oxalic acid solution and rubbed on with a cloth. All residues must be removed and the surface wiped dry with a clean cloth. Abrasives should not be used on highly polished (mirror) surfaces. When buffing compounds have been used in polishing prior to coating, parts should be degreased or otherwise cleaned to remove any residue.

Degreasing is normally done with solvents such as butyl cellosolve and trichloroethylene. To prevent streaking and staining, it may be necessary to wipe-dry large areas with lint-free wipers. Freshly plated parts must be thoroughly neutralized and rinsed in hot water prior to coating.

The spraying area should be free of dust and dirt and at moderate temperature (between 50° and 90° F), at low humidity (certainly less than 80% when organic vehicles are used), and well ventilated.

Usually enough coats are applied to achieve a total dry film thickness of 0.5 to 1.5 mils. Greater thickness tends to become obvious and the metal takes on a varnished appearance. However, the coating manufacturer may recommend thinner coatings for certain applications.

## Coating Properties

The properties of a number of proprietary commercial coatings are presented in Table 1. Properties of a coating are sometimes dependent on the composition of the substrate (copper, brass, nickel-silver etc.). The properties shown in Table 1 are representative of those found on several different substrates. This compilation illustrates that the differences among coatings of a given organic base can be as great as the differences among the bases. The differences arise because the manufactures use their own formulations, combinations of polymers, and additives.

The test procedures used to compile the properties in Table 1 were as follows:

**Pencil Hardness** – Hardness at which transition from scratching of the coating to crumbling of the lead occurs. The scale of hardness from hardest to softest is 7H, 6H, 5H, 4H, 3H, 2H, H, HB, F.

**Taber Abrasion Test** – A CS 10 Calibrase wheel with a 500 gram load was run on the specimen to failure or to 500 cycles. Results are reported as loss in weight due to abrasion.

**Flexibility** – Bending was done over a 1/8 – in. to 1 ½-in. Gardner conical mandrel. Results are reported as no cracking (NC), fine cracking (FC), cracking©, or severe cracking (SC).

**Impact Resistance** – A 28 inch-pound impact was performed on a Gardner Impact Test. Results are reported as no starring (NS), slight starring (SS), starring (S), or extensive starring (ES).

**Resistance to Chemicals** – Samples were visually examined to detect changes after exposure to solutions used were 0.5% ammonium sulfide, 1% Tide detergent, and synthetic perspiration.

## Additional Considerations

A lustrous metallic surface acts as an excellent back drop to view coating defects and tarnished spots. Therefore, the tolerance for defects is low and clear coatings must have a high degree of effectiveness in order to perform satisfactorily. This is less of a problem on antiqued or colored metals. Of concern on copper alloys is that darkening of the substrate can occur even under a coating that is intact due to interaction of the copper with residual solvents. This is a special problem during outdoor exposures when ultraviolet radiation can stimulate the breakdown of solvents. By proper choice of solvents and additives this problem can be minimized. Ethyl alcohol and isopropyl alcohol cause considerable tarnishing. Benzene, toluene, xylene, butyl acetate, and ethyl acetate are much better.

Discoloration of copper and its alloys also may occur at the curing temperatures normally recommended for thermoset coatings. It is wise to use low curing temperatures and short curing schedules to avoid such in-process discoloration. Catalytic activity by copper sometimes allows lower temperatures or shorter curing schedules to be used.

Short high temperature baking schedules are a requirement for coil coating operations. A considerable amount of research has been carried out in this field and satisfactory coil coating formulations are available. These coatings can be formed after curing and still retain good protective properties. The use of a Tedlar film for coil coating is a new innovation. The extremely long life of Tedlar coatings in outdoor applications provides savings in maintenance expenses which may justify the added expense of coating. Tedlar coated metal also may be formed.

Adhesion of coatings to copper and its alloys can be a problem. Considerable research is underway in this area also. This work has shown that adhesion of coatings can be improved by the use of primers or conversion coatings. In coil coating operations pretreating solutions may be sprayed on and dried before coating. However, pretreatments have been known to affect the formability of the coating and this must be checked before a pretreatment is adopted. Pretreatment may also be used to provide protection against under-film tarnishing by incorporating inhibitors on the solutions or preoxidizing the surface.

## TABLE 1. Representative Properties of Clear Coatings on Copper Metals

| Coating Family* | Pencil[(1)] Hardness | Taber [(2)] Abrasion Resistance (mgs) | Flexibility[(3)] Conical Mandrel | Impact[(4)] Resistance | Resistance[(5)] to Chemicals |
|---|---|---|---|---|---|
| AIR DRYING | | | | | |
| Nitrocellulose | HB | Fail 400 | NC | NS | |
| Cellulose Acetate Butyrate | HB | >40 | NC | S | Poor in sulfide |
| Cellulose Acetate Butyrate | HB | 26 | NC | S | poor |
| Cellulose Acetate Butyrate | H | Fail 300 | SC | ES | |
| Cellulose Acetate Butyrate | HB | 35 | SC | ES | Poor in sulfide |
| Acrylic | 2H | 25 | FC | SS | Poor in sulfide |
| Acrylic | 2H | >50 | NC | NS | |
| Acrylic | HB | Early failure | NC | SS | Poor in sulfide |
| Acrylic | HB | 25 | C | SS | Poor |
| Urethane | 2H | 15 | NC | SS | |
| Urethane | HB | 20 | FC | NS | Poor in sulfide |
| Urethane | HB | 10 | NC | NS | Excellent |
| Urethane | HB | 2 | NC | NS | Excellent |
| Polyester-Epoxy | HB | 25 | NC | NS | Excellent |
| Silicone-Acrylic | HB | 30 | C | ES | |
| Phenolic | H | 13 | C | ES | Poor |
| Phenolic | HB | 25 | FC | NS | Excellent |
| Cellulose Acetate Butyrate-Alkyd | F | 35 | NC | ES | |
| Vinyl-Butyral | HB | 25 | NC | SS | |
| Vinyl | HB | 20 | NC | NS | Excellent |
| THERMOSETTING | | | | | |
| Acrylic | 2H | 1 | C | S | Fair |
| Acrylic | 3H | 8 | C | SS | Excellent |
| Acrylic | 4H | 13 | FC | SS | Excellent |
| Acrylic | H | 22 | NC | NS | Excellent |
| Epoxy | 6H | 2 | C | S | Excellent |
| Silicone Alkyd | HB | 63 | C | SS | Excellent |
| LAMINATE | | | | | |
| Polyvinyl Flouride | H | NC | NC | NS | Excellent |

* The properties presented here are representative of proprietary formulations involving the polymers listed.

(1) The scale of hardness from hardest to softest is 7H, 6H, 5H, 4H, 3H, 2H, H, HB, F.

(2) Weight loss in milligrams after 500 cycles with a CS 10 Calibrase wheel and 500 gram load.

(3) Bent on a 1/8-in. to 1 ½-in. Gardner Conical Mandrel. Results are reported as no cracking (NC), fine cracking (FC), cracking (C), or severe cracking (SC).

(4) a 28 inch-pound impact on a Gardner Impact Tester. Results are reported as no starring (NS), slight starring (SS), starring (S), or extensive starring (ES).

(5) Solutions used were 0.5% ammonium sulfide, 1% Tide detergent, and synthetic perspiration.