PHIBRO-TECH, INC.

COPPER STRIPPING PROCESS AND RECYCLING OF WASTE STRIPPER
PHIBRO-TECH, INC. RIDGEFIELD PARK, NJ

Many companies that are stripping plated copper used as a heat-treat mask have converted to ammonia-based products in place of cyanide, chromic acid, or nitric acid. This presentation will review the development of the ammonia stripping process, its effectiveness and speed of copper removal, other stripping process issues, and the recycling of waste stripper solution.

Process History

The ammoniacal process to strip copper heat treat mask from plated parts has its roots in the copper mining and refining industry.

Ammoniacal solutions were once used extensively to leach copper from ore.

The ammoniacal leach solution can hold over 16 oz/gallon copper. The copper saturated ammoniacal leach solution can then be electro-refined to produce copper cathode. The copper depleted ammoniacal solution is then replenished with ammonia and recycled back to the ore leaching system.

Copper can also be recovered from ammoniacal copper leach solutions via solvent extraction technology. Mining and refining ammoniacal leach solution systems use millions of gallons, operated on a huge scale. The same principle has been downsized for use in metal finishing operations.

The advantages of ammoniacal copper leach solution; high copper loading and speed also apply to the use of ammoniacal solution to strip copper heat treat mask from plated parts.

The waste ammoniacal copper strip solution is readily used to manufacture several copper compounds, including Copper Oxide and Copper Sulfate. The ammonia is also recovered for re-use in manufacturing several ammonia compounds, including Ammonium Chloride and Ammonium Hydroxide.

During the past 25 years several U.S. companies have built plants to produce ammoniacal copper strippers. Some of these suppliers also recycle the waste material.

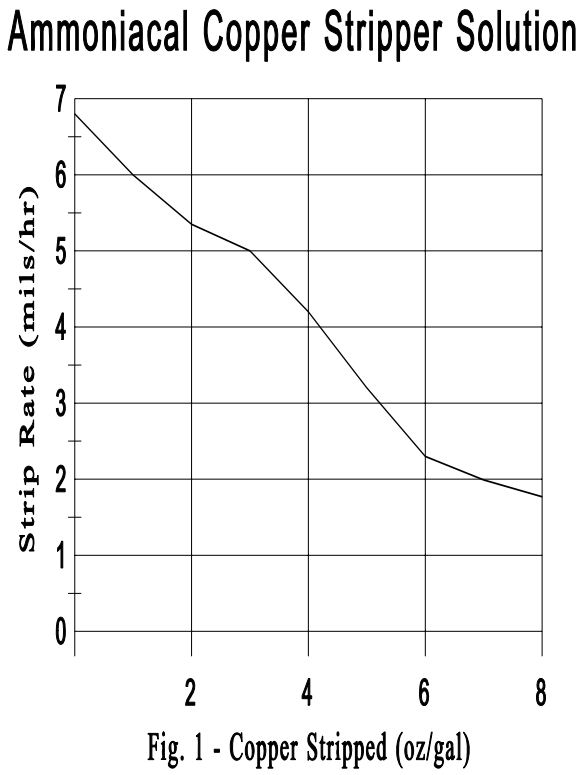
A similar manufacturing and waste recycling infrastructure exists in Europe and is being developed in Asia.

Process Parameters

Fresh ammoniacal copper strippers have been shown to strip one mil of copper in 10 to 15 minutes vs. 3 hours for cyanide-based chemistry.

One Midwest aerospace gear manufacturer is able to get more productivity from one ammoniacal strip tank than had previously been obtained from four cyanide strip tanks.

Ammoniacal strippers can hold up to eight ounces per gallon of copper, while cyanide-based solutions are usually dumped at about two ounces per gallon.



Even as the copper concentration of a working ammoniacal stripper approaches eight ounces per gallon, the strip rate is still over one mil per hour (figure 1).

Ammoniacal solutions strip copper by immersion. Parts can be hung on plastic coated hooks or placed in plastic or coated baskets or barrels. The strip tank should also be plastic. High-grade stainless steel can also be used for the tank and barrels.

Ammoniacal strip solutions require only low speed mechanical agitation for racked parts. The rotation of baskets or barrels provides sufficient agitation.

Parts should be kept off the bottom of strip tanks. Precipitated copper salts may form at the bottom of older baths, possibly causing etching of the steel, if the parts are on the bottom.

Most ammoniacal copper strippers are two component processes. One component contains ammonia and the second contains an oxidizer. The two components are mixed according to supplier instructions and the bath started. As copper dissolves in the bath, the cupric ions now present actually aid in stripping more copper. As a result, most suppliers do not recommend adding any additional oxidizer component during the life of a bath.

Most ammoniacal copper strippers operate at room temperature and a pH of 9.0 to 10.5 Maintaining proper pH is the most important control parameter.

A working bath will gradually lose ammonia through evaporation. Ammonia is also consumed as copper dissolves, forming a copper-amine complex. As a result, the pH will begin to drop along with a slight reduction in strip rate. The pH can be elevated, by making additions to the

bath of the ammonia component, restoring the strip rate. Excessively low pH can also cause etching of the steel.

The copper strip rate can be increased by elevating the temperature, although there are some disincentives to do so. At higher temperatures more ammonia gas will be liberated, which will lead to excessive chemical consumption and possibly increased worker exposure to ammonia fumes. Higher temperatures also increase the potential for etching the steel parts, particularly in older baths and when carbon steel is being stripped.

In virtually all situations room temperature operation is recommended.

Prior to copper strip the parts must be free of grease and oil. Heat treat scale must also be removed. Best results are obtained when alkaline cleaners and de-scalers are used prior to ammoniacal copper stripping. For carbon steel parts with a heavy copper mask, an alkaline rinse is recommended right before the copper strip bath. An alkaline rinse immediately after stripping is also worthwhile to prevent rusting.

Environmental and Safety

Ammoniacal copper strip solution is by far the safest process. Cyanide-based products are highly toxic, as are chrome-based strippers. Nitric acid can only be used on stainless steel, so its applications are limited. Nitric acid strippers usually produce toxic NOX fumes, which are also difficult and expensive to control using a fume scrubber.

Ammoniacal strippers do require an exhaust to provide a comfortable work environment. The ammonia fumes are easily scrubbed in water or dilute hydrochloric acid. The spent scrubber solution containing ammonia can often be recycled along with the waste stripper bath by the supplier.

Waste cyanide and waste chrome based copper strippers have no recovery value. Nitric acid copper strippers, while recoverable, have limited use in recycling plants.

The ease of recycling waste ammoniacal copper stripper contributes to the much lower cost for removal of spent bath compared to the alternative strippers.

In drum quantities waste cyanide strippers can cost up to $15.00 per gallon for disposal. Chrome-based products cost over $5.00 per gallon for disposal.

Ammoniacal copper stripper waste is generally recycled at a cost of under $2.00 per gallon.

Since ammoniacal copper strippers hold four times as much copper per gallon as cyanide strippers and twice as much copper per gallon as chrome strippers, the waste disposal cost differential is actually much greater per ounce of copper stripped (figure 2)

Copper Strip Solution	Ounces Per Gallon Copper	Disposal Cost Per Ounce of Copper
Cyanide	2	$7.50
Chrome	4	$1.25
Ammonia	8	$.25

(Fig. 2)

Future Work

In the printed circuit board industry ammoniacal solutions have been used to remove unwanted copper from the board, producing the desired circuit pattern. In the circuit board industry, the ammoniacal stripper solution (known as an etchant) is operated at an elevated copper content. Steady state bath conditions are maintained via an automated feed and bleed system for fresh and waste chemistry.

The automated feed and bleed process has only been tried to a very limited extent for stripping copper heat treat mask. The automated feed and bleed process may be appropriate for high volume barrel or basket type operations. This will be more fully investigated in the future.

Conclusion

Ammoniacal solutions to dissolve copper have a long history of varied uses in industry.

For stripping copper heat-treat mask, ammoniacal solutions provide increased speed, process efficiency, economy, worker safety, and waste minimization through recycling. These attributes are unmatched by alternative stripper chemistries.

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