Color Sorting Aluminum Alloys For Recycling—Part II

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A quick and inexpensive way to sort samples or scraps of mixed wrought aluminum alloys according to their alloy series has been developed. Chemical treatments are used to produce a unique color for each series. This method can be used on shredded aluminum scrap so that alloys are recycled more efficiently rather than blending the mixture together for castings. Part II reports on the use of specific tests to differentiate 5xxx and 6xxx alloys and will summarize a successful overall approach.

This is a continuation of the previous article on the separation of aluminum alloy scrap for recycling by imparting a distinctive color to each alloy. Methods of sorting by a caustic or acid etch to provide a distinctive color were discussed. The techniques were able to separate 2036, 3003 and 7003 alloys, but 5754 and 6022 were sometimes separated from the others as a single group because of their lack of coloration by the methods used. Differentiation between 5xxx and 6xxx is desirable for the most efficient sorting of alloys.

The first approach taken to more clearly separate 5754 from 6022 was to investigate various known colorimetric reactions for detecting silicon or magnesium, which are the principal differentiating components of the two alloys. Differences in the concentrations of silicon or magnesium in the two alloys was thought to have the potential to result in coloration differences in the metal surface when exposed to the reagents in question.

Because samples must generally be cleaned of grease, dirt, oxides and paint, the previously defined cleaner and 15-percent caustic treatment used to separate the 5754 and 6022 alloys from the others, was used as the pre-treatment for separation of 5754 from 6022. Thus, the initial separation of the 5xxx and 6xxx alloys from the others can also prepare those two alloys for further reaction by exposing a clean surface containing silicon and/or magnesium, and possibly also silicates or magnesium hydroxide for reaction with the reagents selected.

Unsuccessful Differentiation of 5754 & 6022

Because of the lack of success with these approaches, they are described only briefly. External literature[3] claims that 5xxx series alloys turn darker than other aluminum alloys when exposed to vinegar. After immersion in acetic acid or vinegar, however, both alloys remained white metallic. The conditions of the acetic acid tests were 5-pct acetic acid, 100-pct acetic acid, or apple cider vinegar conducted at room temperature, 140 and 180 °F for times up to 10 min. Other chemical solutions were tried based on chemical spot tests as follows:[4]

Molybdate in acid solution is claimed to turn yellow in the presence of silicates. Because there is a silicon content difference in the 5xxx and 6xxx alloys, samples were immersed in molybdate solutions under varying conditions. Samples of 5754 and 6022 were immersed in 20-pct, 160 °F NaOH for 30 sec, or immersed in room-temperature 20-pct hydrochloric acid, or both in sequence prior to being placed in the molybdate solution for one min. Other samples were cleaned only in alkaline cleaner and placed in the molybdate solution. Experiments used 0.1-pct ammonium molybdate at room temperature or 140 °F at pH of 1 or 6. No discernible yellow color differences were produced, however, in any of the experiments. Traces of blue were visible from reduction of the molybdenum by aluminum, but no yellow color resulted from silicon.

Benzoin in the presence of silicate is described as producing a fluorescent complex. Samples of 5754 and 6022 were etched in 15-pct sodium hydroxide at 140 °F for 45 sec and immersed in 0.5-pct benzoin at room temperature for one min, but did not yield any fluorescence.

Magnesium hydroxide is reported to be tinted reddish by iodine solutions, and because there is a difference in Mg concentrations in 5xxx and 6xxx alloys, the iodine solution was evaluated. A KI/I_2 solution was made by dissolving 20 g KI plus 6.4 g I_2 to 100 mL in water. Panels of 5754 and 6022 were immersed in this solution, allowed to stand up to 30 sec and very briefly rinsed (2 sec) in water. This resulted in a slightly darker red color for 6022, but longer rinsing (5 sec) washed away all color in both alloys. Because the color differences did not withstand rinsing, further study of this technique was not pursued.

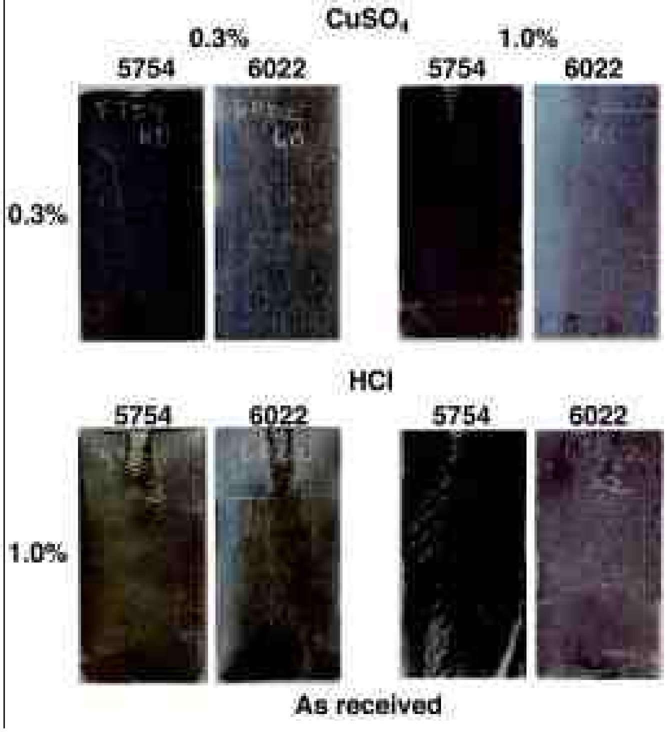

Fig. 3—Photo showing color differentiation of aluminum alloys 5754 and 6022.

Successful Differentiation of 5754 & 6022

Feigl & Anger claim that Mg salts are dyed blue in quinalizarin (1,2,5,8-tetrahydroxyanthraquinone).[4] Alloy 5754 immersed in one-pct quinalizarin at room temperature between 3 and 10 sec dyed a darker purple than 6022 similarly etched. This is an uncommon and expensive dye, however. The successes to this point were marginal or impractical, so original approaches were tried.

Silver ions are reduced to metallic silver on copper metal, so silver solutions were investigated for reduction by aluminum or magnesium in the alloys. It was found that immersion of cleaned and caustic-etched 5754 and 6022 in a 0.5-pct silver nitrate solution at room temperature darkened 6022 more than 5754 after only 10 sec. This indicated a promising theoretical approach. Because the use of silver nitrate could be very expensive on a large scale, further experiments were pursued using copper sulfate, which is still relatively noble, but less expensive and readily waste-treatable.

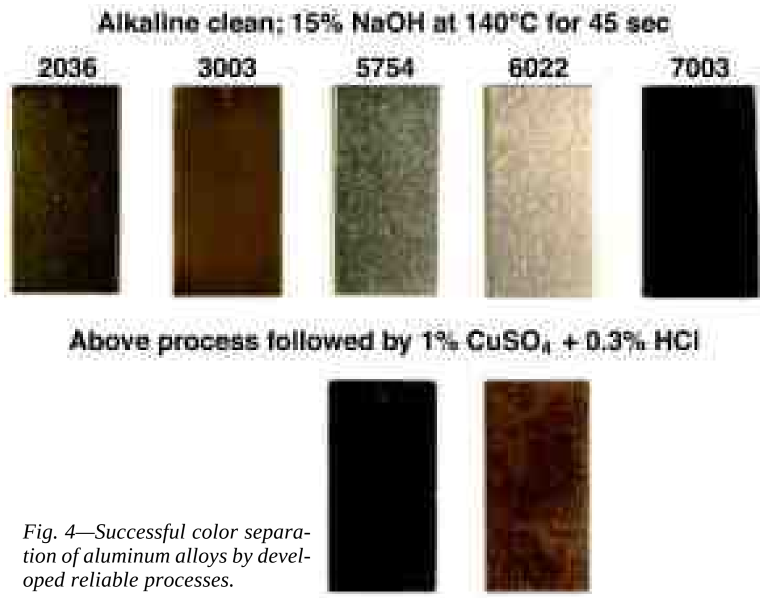

Fig. 4—Successful color separation of aluminum alloys by developed reliable processes.

Immersion of 5754 or 6022 in a copper sulfate solution results in no color change, even though deposition of copper was expected. Pre-treatment of the coupons in cleaners and caustic etches had no effect in aiding deposition. It was concluded that the passive oxide layer that begins to form on aluminum immediately after being removed from the caustic etch could be interfering with the reaction in the $CuSO_4$ solution. HCl was added to the copper sulfate solution, therefore, in an effort to depassivate the protective layer. Solutions examined included 0.3% HCl + 0.3% $CuSO_4$, 0.3% HCl + 1.0% $CuSO_4$, 1.0% HCl + 0.3% $CuSO_4$, and 1.0% HCl + 1.0% $CuSO_4$. Chemical treatments of 5754 and 6022 in the copper sulfate plus HCl were found to darken both alloys with gray-red copper deposits. It was further found that under proper conditions, the color of the copper deposits is sufficiently different for the two alloys that reliable differentiation appears to be possible. This is described in the table and shown in Fig. 3. The conditions resulting in the most distinct appearance difference for 5754 and 6022 is the 1.0% $CuSO_4$ with the 0.3% HCl etch. Neither solution with the more concentrated 1.0% HCl provided as discriminating a color difference.

It is important to note that the color of the copper sulfate treated samples varies with the angle of observation. Colors from deep red to reddish gray are observed in the same sample, depending on whether observed at a high or low angle. Regardless of the reflection angle, the alloys have a differentiable appearance.

Selection of Separation Techniques

All of the colors generated, except the I_2-generated colors, do not wash away in mild running cold water rinses. Some, however, particularly the NaOH-etched 3003, may have the color abraded away by very strong spray rinses or mechanical abrasion.

Of all experiments tried, 1% $CuSO_4$ + 0.3% HCl yields the greatest color difference between 5754 and 6022. It is also the most practical set of conditions, inasmuch as the iodine washes away quickly, the silver is expensive, and the quinalizarin is both expensive and may be more difficult to waste-treat. This test, combined with the caustic etch, enables differentiation of each of the alloys of interest.

Simultaneous immersion of all of the automotive alloys tested into the copper sulfate/hydrochloric acid mixture does not enable clear differentiation of the alloys. Alloys 2036 and

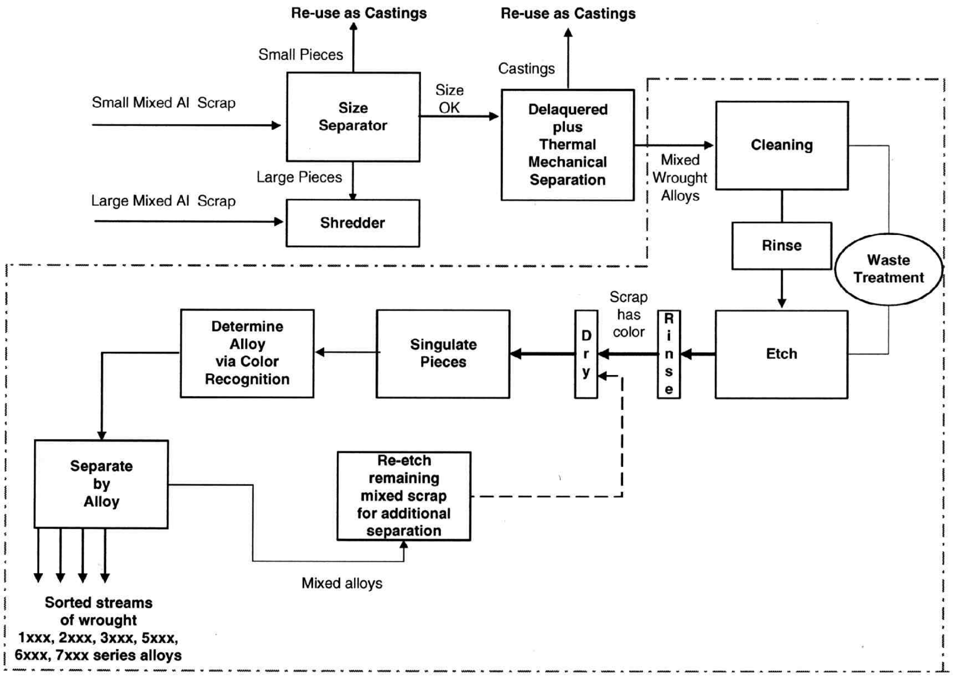

Fig. 5—Detailed flow diagram of commercial scrap sorting plant. Processes include thermomechanical separation with concomitant delacquering, as well as color sorting.

Material Appearance of Automotive Alloys 5754 & 6022 After Chemical Etching with $CuSO_4$ & HCl

	0.3% HCl	**1.0% HCl**
0.3% $CuSO_4 \cdot 5H_2O$	5754 Med Gray 6022 Lt Gray	Both Med Gray
1.0% $CuSO_4 \cdot 5H_2O$	5754 Med-Dk Gray with Red 6022 Lt Gray with Red	5754 Med-Dk Gray 6022 Med Gray with bit of Red

3003 both come out white, but 5754, 6022 and 7003 have differentiable colors (dark gray, light gray, and medium gray, respectively). Immersion of the automotive alloys into caustic solution, followed by copper sulfate/hydrochloric acid without first sorting and removing the 2036, 3003 and 7003, results in an irregular fading of the colors generated by the caustic on the 2036, 3003, and 7003. Such irregular shading may create problems with the color sorting equipment. Moreover, the 3003 and 5754 have very similar irregular reddish colors.

The most reliable process is therefore to immerse all series in the sodium hydroxide solution, separate the 2xxx, 3xxx, and 7xxx, immerse the mixed 5xxx and 6xxx in a copper sulfate/hydrochloric acid mixture, and separate the 5xxx and 6xxx alloys. The resulting colors are shown in Fig. 4.

The resulting flow scheme is shown in Fig. 5. Incoming scrap includes shredded scrap, mixed large chunks of scrap, and small turnings from machining. Large pieces of scrap would go through a shredder to be sized appropriately for subsequent automated handling. Small scrap would be screened to separate pieces too small to justify further separation from the large-volume pieces. The small scrap would be remelted for use in the casting industry, much as is done today with mixed scrap. The appropriately sized scrap would be thermally delacquered to remove any paints and adhesives. During the delacquering process, a thermomechanical separation like that developed by the U.S. Bureau of Mines[1,2] is expected to be carried out to separate castings from the wrought scrap. The castings will be diverted for re-use in the casting industry. Following delacquering and separation of the castings from the scrap mix, the wrought scrap will be cleaned, rinsed, etched in caustic, rinsed, and possibly dried. The chemical treatment will impart a color to the scrap which is dependent on the alloy composition. The colored scrap pieces will then be separated and aligned on conveyor belts for presentation to an optical sensor. The optical sensor would classify the scrap according to color, which is a reflection of major compositional differences corresponding to alloy families (i.e. 2xxx, 3xxx, 5xxx & 6xxx and 7xxx series alloys). Signal output from the optical sensor will control the mechanical separation of the scrap into scrap streams defined by alloy family. The group of 5xxx and 6xxx alloys will be processed again in the copper sulfate/hydrochloric acid bath and re-enter the color recognition portion of the line for final sorting.

Additional Experiments & Observations

Other aspects of all of the above processes are noted here. They include observations of practical limitations and generally applicable techniques and influences:

Heat treatment of the alloys has some minor effect on the resulting colors, but overall results are generally the same, and alloys remain differentiable. Alloy 5754 recrystallized with a very large, visible grain structure, but color differentiation from 6022 remains possible when using 1% $CuSO_4$ + 0.3% HCl.

Surface roughness or lack thereof on samples can influence the apparent color seen by the naked eye to a limited extent.Sandblasting, ball milling, or other mechanical surface treatment of the alloys prior to chemical treatment can be used to make surface topographies of different samples similar, so that colors will be less influenced by surface textures. In all of the successful experiments noted above, however, color differences between alloys were sufficiently great that changes in surface topography would not influence sorting.

Transfer time, the time between removal of samples from a coloring bath and the beginning of a rinse, can be important, especially in the heated solutions. After 180 °F in NaOH, samples allowed to begin drying in air for five sec before rinsing are rendered non-uniform in color because of air oxidation of the metal surface. Samples should be rinsed in less time than that at which discoloration begins as a result of dried-on solutions. In the case of 180 °F NaOH, this may be as little as two sec.

Consideration was given to the reaction mechanisms responsible for the above colorations, but definitive answers were not always possible within the scope of the work. X-ray photoelectron spectroscopy was performed on the surface of the aluminum samples etched in 15% NaOH and those treated with copper sulfate/hydrochloric acid. Results show many elements as would be expected from the alloy compositions, such as heavy copper deposits in the 2xxx series samples, manganese in the 3xxx series, and zinc on the 7xxx series. Other results were more difficult to explain, such as substantial copper deposited on the 3xxx series etched in caustic. Large amounts of zinc on the caustic etched 7xxx alloys suggested the immersion re-deposition of zinc as soon as it was dissolved, similar to the deposition of zinc onto aluminum in a sodium zincate bath. Deposition of copper, or an oxide or hydroxide thereof, or leaving behind a residual smut of copper, is the likely cause of 2xxx alloys darkening in the caustic bath.

After immersion in the copper sulfate/HCl, the 5754 alloy had substantially more residual copper by XPS measurement than the 6022. Electrochemical potential differences between the 5754 and 6022 alloys would most easily explain the color differences in the copper/HCl experiments, but no significant electrochemical potential difference was found when measured. The potential was measured on the entire coupon, however, and localized differences at individual grains could conceivably result in the color differences. Ultimately, it was considered beneficial but not necessary to explain all of the results theoretically, but detailed explanations require more extensive study. Additional approaches to differentiation of the alloys are possible, including the use of oxidizing agents, chelators, ammoniacal solutions, and other reagents, either alone or in combination with the materials used above. It was not found to be necessary to use these additional approaches at this point, but they should be considered for future use if needed.

Very limited experiments suggest that casting alloys could potentially be separated by the caustic etch technique, both from each other and from wrought alloys, but the success of this will depend heavily on the various alloys being sorted. In practical terms, there is substantial benefit from thermal presorting of the castings in that (1) the surfaces are also delacquered in the thermal step, (2) the volume of scrap to be chemically treated is reduced by thermal sorting, and (3) less alloys in the color sorting step will result in fewer technical difficulties in sorting them. Alloy segregation causing compositional differences within a casting will potentially play a significant role in the success of sorting cast alloys.

Waste Treatment

Waste treatment of the etching solutions was not experimentally investigated, but some projection of possible schemes is possible. The solutions proposed are generally similar to existing metal finishing solutions. Crystallization is a common approach to rejuvenation of caustic etches. The resulting aluminum trihydrate by-product is sometimes sold. Rinsewaters may be purified by reverse osmosis or ion exchange and reused as rinsewater. The concentrated caustic or copper sulfate solutions separated from the rinsewater by these processes can be returned to their respective etching steps. Ultimate disposal of the copper ions after final use of the copper sulfate solution could be done by (1) concentration of the copper by reverse osmosis or ion exchange columns, and (2) plating the copper from concentrate. The plated copper metal could be sold for recycling. Ultimate disposal of the sodium hydroxide and hydrochloric acid solutions would involve mutual neutralization. Sodium hydroxide for disposal can be used to neutralize similarly disposable hydrochloric acid to form simple salt water.

Some Key Unanswered Questions

Many questions remain, but some key ones include the level of contamination/by-products the solutions can tolerate (*i.e.*, solution life), and what are the optimum operating parameters (forthis or other alloy groups). Engineering and operating factors will influence the answers, which must wait until an engineering design has begun. This work must be considered only to be proof of concept, and not a final sorting scheme ready for large-scale implementation.

Conclusions

A reasonable two-step chemical treatment to enable color separation has been discovered. The process consists of the preliminary steps of delacquering and otherwise cleaning the scrap to expose metallic surfaces. The chemical treatment steps are:

- Etch in approximately 15% NaOH for 30-60 sec at 140 to 180 °F; separate 2xxx, 3xxx and 7xxx alloys from scrap stream, leaving 5xxx and 6xxx alloys commingled.
- Immerse the commingled 5xxx and 6xxx alloys in a copper sulfate/ hydrochloric acid solution and separate the 5xxx from the 6xxx alloys.

Note: A patent application has been filed for this coloration process for sorting aluminum alloy scrap.

Editor's note: *Because of a scheduling error, Part II did not appear in the May issue. Part I appeared in the April 2000 issue.*

References

3. *Recycled Metals Identification and Testing Handbook*, National Assoc. of Recycling Industries.
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