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THE USE OF THE ALONIZING PROCESS IN
SULFURIC ACID PLANT CONSTRUCTION^{1/}

W. A. McGill* and M. J. Weinbaum**

* Applications Engineer, Alon Processing Inc., Tarentum, Pa., USA

** President, Alon Processing Inc., Tarentum, Pa., USA

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INTRODUCTION

The increasing use of fertilizers throughout the world is too well-documented for any need to repeat or to dwell on at this time. One important aspect of this burgeoning demand has been the derived demand for sulfuric acid and our attention will be focused on the production of the enormous amounts of sulfuric acid required and one means of reducing the pollution inherent in this production.

Today, in the western world, over 50% of all sulfuric acid consumed is used to make fertilizers. Most of this acid is utilized in the manufacture of the phosphate-based fertilizers. To put this in another perspective, total sulfuric acid production in the world went over 100 million metric tonnes for the first time in 1972. About 33% of this total is used in the manufacture of these fertilizers.¹

Thus, the generation of sulfuric acid is an important and a major step in the agri-chemical industry.

I. MANUFACTURE OF SULFURIC ACID AND ATTENDANT POLLUTION PROBLEMS

The modern contact sulfuric acid process, by which over 98% of all acid is produced today, involves the oxidation of a stream of sulfur dioxide gas during one or more passes through a catalytic converter. The sulfur trioxide gas produced is then absorbed in an oleum which is finally diluted to an acid of desired strength. The equilibrium balance of the oxidation reaction is most efficiently maintained if the sulfur dioxide stream is at about 410° C; but, conversion works fastest if the temperature is at about 600° C. A balance of inlet/out temperatures at various passes through the converter is achieved through an ingenious arrangement of gas-to-gas heat exchangers, waste heat boilers, economizers, and/or air preheaters. Through the use of proper arrangement of exchangers in which sulfur dioxide and sulfur trioxide are heated and cooled, efficiency of 97 - 98% can be achieved; i.e. only 2% or 3% of the sulfur dioxide is passed beyond the converter and discharged through the stack into the atmosphere.

The conversion rate of 97 - 98% obtainable in the conventional contact plant is equivalent to 20 - 85 pounds of sulfur dioxide emitted per ton of acid produced, according to the Environmental Protection Agency in the United States. The average is about 40 pounds per ton and, even when the plant is running at lined-out conditions, in other words, smooth operation after start-up problems have been overcome, about 27 pounds of SO₂ per ton of acid produced is considered optimum. Stated

another way, this represents an emission rate of about 2000 ppm and was the standard accepted by most state governments in the United States prior to the passage of the Clean Air Act of 1970.

II. POLLUTION CONTROL STANDARDS AND TECHNIQUES IN THE UNITED STATES

The national standards adopted in 1970 in the United States called for emission levels in new sulfuric acid plant construction to be held at four pounds per ton of acid produced, equivalent to 300 ppm. This assumed a conversion efficiency of about 99.7%. Existing acid plants were to come into compliance within a few years and had then to operate at a 6.5 pound per ton emission rate, a conversion efficiency of 99.5% or 500 ppm. These standards assumed the highest verifiable level of conversion to be found anywhere in new plant construction. The standards assumed, also, that all of the known pollution control devices would be used and even then acid producers were hard-put to feel that these conditions could be met on a regular basis.⁴

The main weapon used in fighting for lower emission levels is the double-absorption principal, also called the double-catalysis process or the inter-pass absorption principal. In the plant utilizing this route, some of the sulfur trioxide is absorbed from the process stream before the final conversion pass. This permits oxidation of even more SO_2 in the final passes and the conversion efficiencies of 99.5% to 99.7% are possible. This level is high enough to comply with E.P.A. regulations in the United States. A prominent feature of the double-

catalysis plant is the addition of one or more large gas-to-gas heat exchangers in the inter-pass stream. These exchangers heat the gas stream after absorption to keep it from condensing. The heating reagent in these exchangers is the sulfur trioxide gas mixture from the converter.

As can be seen, the ability of all systems to run at designed parameters is vital in the operation of the double-absorption plants. The many large heat exchangers are no exception to this rule. According to a spokesman for the industry,

"Particular attention must be paid to design of heat exchanger equipment."⁵

The reason for this is apparent.

The efficiency of the conversion process depends upon (among other things) the inlet/outlet temperatures of the gas stream at the various conversion passes. The design of the interpass unit is particularly critical as condensation of the acid stream at this point must be avoided to prevent catastrophic destruction of downstream equipment. The tubing in the tube and shell exchangers, if made of unprotected carbon steel, will scale very rapidly at the working temperatures in the gas streams to which they are exposed. If these tubes do scale, several damaging conditions result:

1. The plant must be shutdown periodically to remove the scale contamination. Not only is this expensive but shutdown and start-up periods are those of greatest emission levels.
2. The formation of scale impedes heat transfer reducing conversion efficiency. This too increases costs and SO₂ emission levels.
3. The scale increases pressure drop in the unit, causing a further loss of efficiency.

All of these are to be avoided if a plant is to continue to operate as originally designed.

III. THE ALONIZING PROCESS AND ITS APPLICATION

The best way found to eliminate scale formation on the heat exchanger tubes is to have the tubes aluminized. Aluminizing can be performed by hot dipping the tube into a bath of molten aluminum, spray metallizing the surface of the tube with aluminum or diffusing aluminum into the surface of the tube. Spraying or dipping results in a layer of pure aluminum on top of the steel. The layer may or may not have voids depending on the condition of the surface of the tubing before aluminizing and the technique used in applying the aluminum. Also, these methods result in a condition in which a temperature runaway could result in a melting away of the aluminum protection (at temperatures of about 1300° F (704°C) or

above). Finally, these methods of aluminizing are not capable of insuring the integrity of the coating of inside surfaces of long tubes of small diameter.

The Alonizing method overcomes all these difficulties. The process is a pack cementation operation during which aluminum, in a high temperature vapor phase, is diffused into the surface of the tubing. The resultant diffusion zone, since it is not a coating but is rather a true alloy, cannot be lost through accidentally scraping, scratching, abrading or melting away. The diffusion zone, which can protect both the inside and the outside surfaces of the tubing, is about 0.010" minimum 0.254mm thickness and has an aluminum content on the surface of about 55%, making the tubes impervious to sulfide scaling. Fig. 1. Alonized tubes, which are generally ASTM A-178, Grade A welded boiler tubes for sulfuric acid plant exchangers, cost considerably less than stainless tubes and will resist scaling and sulfidation better than stainless steels. Additionally, Alonized carbon steel has about 2-1/2 times the thermal conductivity of stainless steel tubing.

Since Alonized tubes will not scale, several important economies can be realized. First of all, it is never necessary to shutdown the plant to clean the exchanger. In acid plants equipped with unprotected carbon steel tubes, cleaning becomes necessary every 2 - 5 years. The size of the exchangers built today will make it impossible to remove all the sulfide scale even during a full plant shutdown.

Meanwhile, the accumulation of scale while the plant is on stream will lower efficiency through reduced heat transfer even before the condition calls for a plant shutdown. The loss of efficiency can be detrimental to the conversion rate and can be a contributing factor to equipment breakdown and increased emission levels.

Alonized tubes are found in plants in twelve countries and on every continent in the world but they have been used most frequently, since the late 1960's, in the United States. The need for the use of these materials has been enlarged in the United States by the passage of the Clean Air Act of 1970 which in effect made necessary the use of the double-absorption process plant with the large heat exchanger elements involved.

The first two double-catalysis plants built in the United States both used Alonized tubes, as has been true of almost all subsequent plants built in that country. A third plant was rebuilt to comply with the Clean Air Act at the beginning of 1970 when the effects of the legislation were first being felt.

It would be instructive to examine these first three plants in some detail.

A. NL Industries

The Titanium Pigments Division of NL Industries (formerly National Lead Company) operated an acid plant in St. Louis, Missouri. Faced

with a difficult pollution problem and threatened with a multi-million dollar suit because of noxious stack emissions, management decided to contract for a completely redesigned unit. The plant, engineered and built by Davy Powergas (then Wellman-Lord), utilizes the Lurgi process for its double-absorption principal. The total plant cost was well over \$5 million and capacity is 300,000 tons per annum.

Prior to installation of the double-absorption plant in St. Louis, NL Industries had used Alonized tubes in the hot exchangers of their metallurgical acid plants in all other locations. Many of these tubes had been in use for years. This company had first tried spray-metallized tubes but with limited success. Then Alonized tubes were used and had been running clean and without scale for over ten years at the time of the St. Louis construction.

Four years after the installation of the double absorption plant there is still no evidence of any scaling of the tubes in the NL Industries operation in St. Louis.

B. American Cyanamid

Cyanamid's Warners plant, rated at 210,000 tons per annum capacity, was the first installation in this country to utilize the Bayer double-absorption process, licensed to Monsanto Enviro-Chem Systems. It is an elemental sulfur burning plant. Building permits for this plant were issued by the state of New Jersey, prior to the passage of the National

Clean Air Act; but, the New Jersey requirements were such that any prospective sulfuric acid plants had to embody the latest available advances in pollution control equipment and techniques before construction licenses could be granted.

This plant was designed to hold sulfur dioxide emissions to less than 500 ppm, thus achieving a conversion efficiency rating of 99.5% and put the plant in full compliance with the strictest version of the national act. This plant has now been in operation for over five years with Alonized exchanger tubing and emission rates on the order of 230 ppm are being achieved on a regular basis. There has been no scale accumulation in the heat exchanger since this plant was on stream.

C. Olin Corporation

The third plant was brought into compliance with the Clean Air Act by Olin Corporation in Paulsboro, New Jersey. The factory was an old one when purchased by Olin and emissions were so bad that they sometimes interfered with normal activity at Philadelphia's International Airport across the river from Paulsboro.

The existing exchangers were retubed with Alonized steel tubing and a sodium sulfite-bisulfite scrubbing system and mist treaters were put in place to reduce opacity of stack emissions.

This combination of pollution control devices was successful in achieving conversion rates of 99.5% and put this plant, also, in compliance

with the Clean Air Act of 1970.

Since this time, some 32 other acid plants, most producing sulfuric acid to make the phosphatic fertilizers, either have gone on stream or are in the process of being constructed using Alonized tubes in the appropriate heat exchangers.

IV. FABRICATING TECHNIQUES

Heat exchangers and other components involving the use of Alonized materials can be fabricated and assembled by use of standard practices.

Most of the gas-to-gas heat exchangers in use in the sulfuric acid industry are assembled through the use of rolling techniques. In general, normal standard practice, as called for in the TEMA (Tubular Exchanger Manufacturers Association) specifications are used even though the exchangers involved do not fall within the framework of the TEMA design. The processor will protect the outside end of the tube where it passes into the tubesheet so that there is no aluminum diffusion in that area and so that roller expanding is performed on bare metal. This helps to insure a good seal and ease of fabrication and assembly. The fabricator should confine his rolling activities to the area of the tube covered by the thickness of the tubesheet and not permit any free expansion to occur. Fig. 2.

Since the Alonizing operation causes a slight dimensional growth of

the outside of the tube, a consensus of manufacturers has come up with a suggested list of hole sizes for various tube dimensions. These have been found to provide necessary clearance for the assembly operation and also provide a good fit for the tubes when they are rolled.

Appendix I, entitled "The Roller Expanding of Alonized Tubes" and Appendix II entitled "Suggested Tubesheet Hole Sizes To Be Used With Alonized Tubes", are a part of this paper and review proper techniques for rolling and suggested sizes for drilled holes.

While rolling is most commonly used, welding of Alonized components can be performed without damage to the integrity of the diffusion zone adjacent to the weld. In this regard, it is important to remember that the iron-aluminum mixture is a true alloy and, therefore, the aluminum cannot be lost through melting as would be the case during welding with other aluminizing operations. The only precaution that must be taken is to be sure that the interface of the weld area is free of aluminum before the welding operation is started. Alonizing should be left off the area which will subsequently become the substrate of the weld to make sure no "tramp" aluminum is present. The reason for this is that aluminum in the interface will be diluted into the weld itself causing a change in the weld characteristics.

V. CONCLUSION

With the large increase in demand for sulfuric acid occasioned by the

ever-greater need for the phosphate-based fertilizers, the potential for sulfur dioxide emission and pollution becomes ever-more a problem. Regulatory agencies throughout the world are interested in holding air quality standards as high as possible, and, to this end, have imposed very strict standards on the permissible emission levels. In order to achieve these levels, it is essential that the plant be designed and run at optimum conditions throughout insofar as clean and efficient service is concerned. The operation of the gas-to-gas exchangers can be maintained at a level of high efficiency and economy of operation throughout the useful life of the plant if the tubes in the exchangers have been Alonized. Since this approach also involves an economy in initial purchase price over the next-best material, it has come into general use throughout the world for modern contact sulfuric acid plant construction.

THE ROLLER EXPANDING OF ALONIZED TUBES

1.0 SCOPE

This specification is intended to provide the required techniques for rolling expanded Alonized tubes into heat exchangers. Both the methods and the equipment specified here are intended to be used primarily for heat exchangers operating with pressure differential across the expanded joints of 75 psig or less. Higher pressures can be accommodated, but they require more extensive hole preparation, a shorter expanded length, etc.

2.0 DIMENSIONAL REQUIREMENTS

Tube hole diameters and tolerances shall be in accordance with the requirements of the Standards of Tubular Exchanger Manufacturers Association (TEMA), latest edition, except that a suitable additional allowance may be permitted to account for variations in the tolerance of the Alonizing as well as for dimensional changes produced by the Alonizing process. In no case, however, should the hole diameter exceed the diameter of the Alonized portion of the tube by more than .030 inch.

Tubesheet drilling tolerances and maximum tube gages shall be in accordance with TEMA recommendations. While shop practices of the manufacturer will govern, Alon will be glad to suggest hole sizes and tolerances if requested.

3.0 EXPANDED LENGTH

For TEMA requirements, the tubes shall be expanded into the tubesheet for a length no less than $.5d + 1/8"$, where d is the nominal outside diameter of the tube before Alonizing. In all cases, the expanded length must be at least $1/16"$ less than the tube sheet thickness, never longer.

4.0 TUBE EXPANSION TECHNIQUES

The technique used for expanding the tubes shall be one which, to the greatest possible degree, avoids both under-rolling and over-rolling. The former, because of inadequate plastic flow at the tube-tubesheet interface, will result in extensive leaks during hydrostatic test and require an excessive amount of rerolling to produce a tight unit. Over-rolling may result in distortion of the tubesheet ligaments, leading to unseating of adjacent tube joints and excessive tubesheet radial growth. The over-rolled condition, once past a certain point, can be extremely difficult to cure, since additional rolling to tighten individual leaks only worsen the general situation. For these reasons, the rolling technique shall be one that

utilizes automatic control of the tube expansion rather than depending on the skill of the operator for consistent results. Furthermore, because of the substantial variations in hole diameters and tube wall thicknesses normally encountered in the fabrication of tubular heat exchangers, rolling processes which are designed to produce consistent tube inside diameters in the expanded region will necessarily result in overexpanded joints (in cases of thick-walled tubes and/or small holes) and/or underexpanded joints (for thin-walled tubes and/or large holes). Therefore, the rolling technique used shall be one which automatically controls the degree of expansion, by, in effect, limiting the torque transmitted to the rolls, independently of moderate variations in tube and hold dimensions.

4.1 CALIBRATION OF EXPANDER CONTROL

Past experience with commercially available automatically controlled tube expanders has indicated that there is sufficient variation among nominally identical control devices and expanding tools so that control settings cannot be established in advance but must be determined on the job, with the particular combination of controller and gun to be used in production. The recommended calibration procedure is as follows:

1. For approximately ten or more of the tube ends, carefully measure the average tube I.D., the average tube O.D., and the average tubesheet hole diameter.
2. For each of the tube ends, calculate the desired tube I.D. after rolling, using the equation

$$d_i' = D - (1 - x) (d_o - d_i)$$

where d_i' = tube I.D. after rolling

D = diameter of hole

d_o = tube O.D. before rolling

d_i = tube I.D. before rolling

x = the predetermined fractional reduction in wall thickness.

The value of x is, to some degree, dependent on the joint material and dimensions, but the value of .04 has been found to give good results over a wide range of tube joint parameters.

3. Set the expander control at a level which, based on past experience, will underexpand somewhat.
4. Expand one tube, measure the average I.D. in the expanded region, and compare the measurement with the value of d_j calculated for that tube in step 2.
5. If the tube is underexpanded, adjust the control for a larger torque and repeat step 4. If it is properly expanded or overexpanded, go on to the next tube, adjusting the control accordingly.
6. When the results for several consecutive tubes indicate that the proper control setting has been found, production expanding can proceed without further dimensional checks. The remaining measured tubes can be used to check the setting occasionally. This can be an important quality control tool, especially when the number of tubes to be rolled is large, since tool wear and other factors can affect the control accuracy.

4.2 ADDITIONAL RECOMMENDATIONS

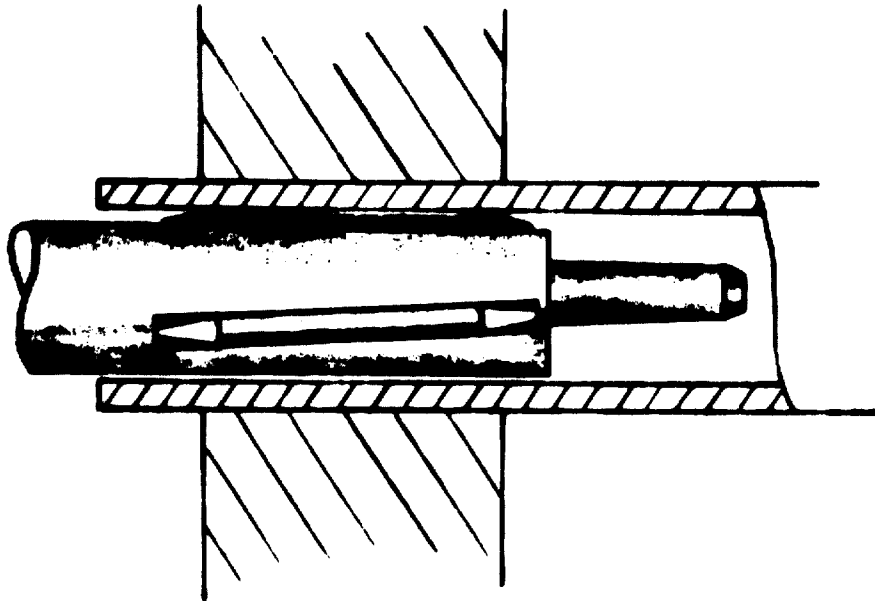
Before adopting a particular expanding tool for production runs, the manufacturer should, of course, satisfy himself that the tool is capable of consistent performance over long production runs and is not overly sensitive to normal variations in tool temperature (which may increase with use), line voltage (for electric motor guns), air supply pressure (for air motor guns), and/or other variable factors inherent in the production situation.

Proper lubrication of the expander rolls is essential to consistent performance as well as to long tool life. While the tool manufacturer's recommended lubricant should normally be used, a light machine oil or a water soluble cutting oil will usually work well. Lubricant can be applied directly to each tube I.D. prior to rolling. In addition, the rolls should be washed frequently to remove metal chips and accumulated dirt particles.

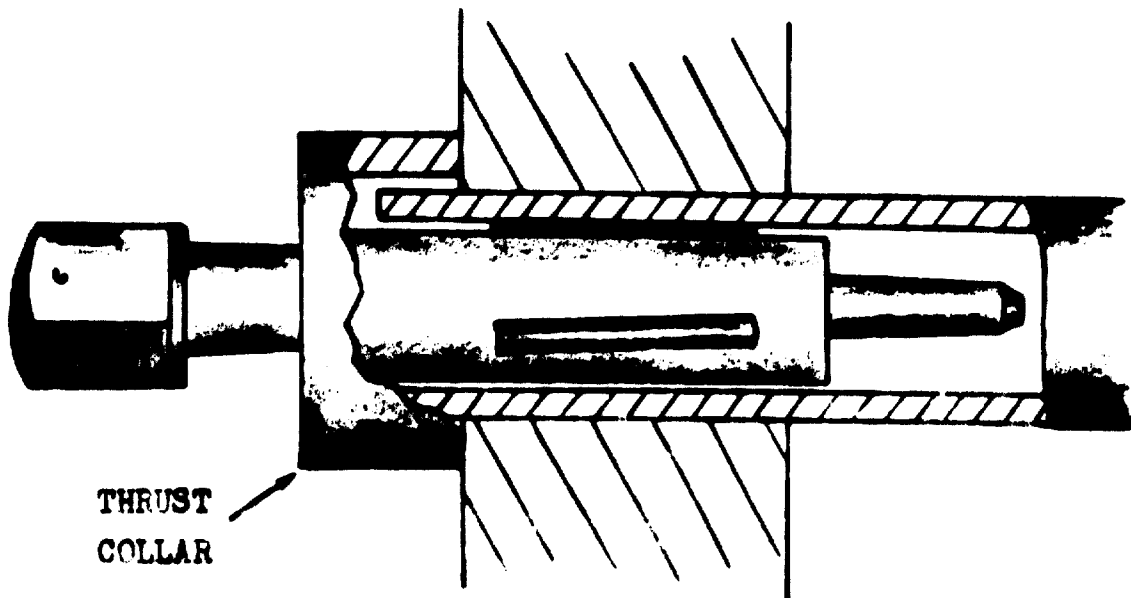
4.3 THE ROLLER EXPANDER

The expander roll length should be at least 1/16" shorter than the tubesheet thickness---never longer.

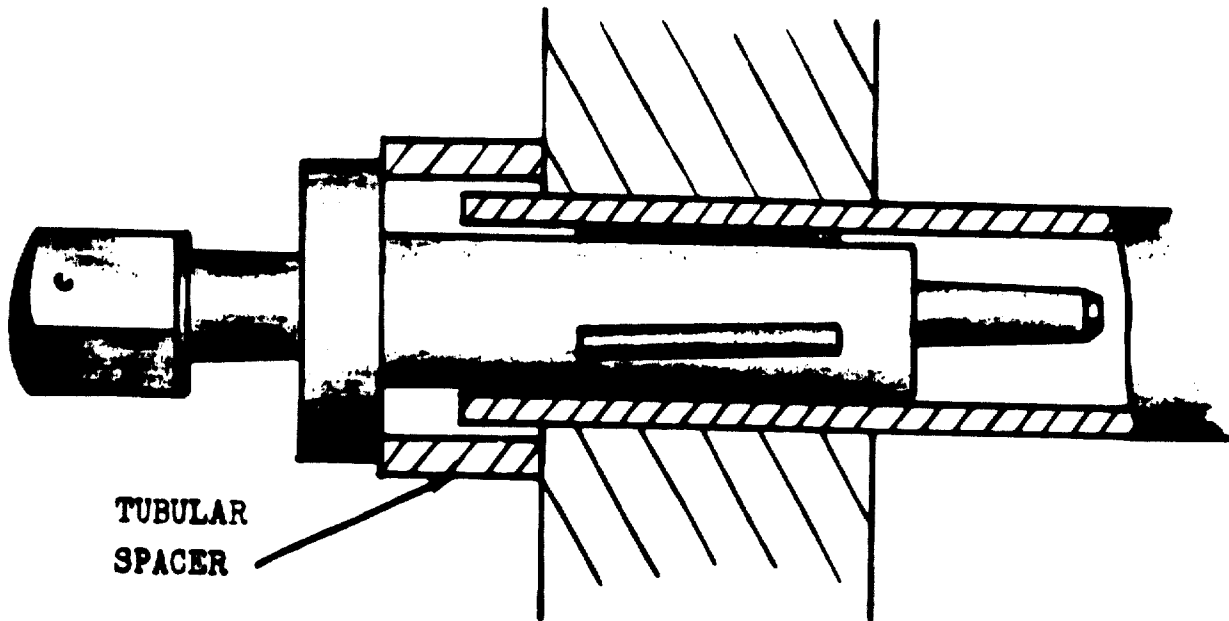
If the correct roll length is not available, remove the rolls from the expander and grind them to reduce the diameter at the areas that protrude beyond the tubesheet. Note on Fig. 1, the rollers have been machined so that the full original diameter lies within the tubesheet hole.



For tubes that extend beyond the open face of the tubesheet, a thrust collar that fits over the tube must be used. The thrust collar positioned against the tubesheet face will accurately locate the expanding rolls within the tubesheet hole. (Fig. 2)



If the expander is not equipped with thrust collar (Fig. 3), a tubular spacer may be improvised with an inside dimension sufficient to accept the tube ends and with a proper length to place rolls accurately within the tubesheet hole.



It is important that free expansion beyond the tubesheet be avoided. Belling or flaring of the tube ends is not recommended. However, if this operation is necessary, proper rolling techniques for the particular tube size will be furnished by Alan.

**SUGGESTED TUBE SHEET HOLE SIZES
TO BE USED WITH ALONIZED TUBES**

Alonizing will alter the dimensions of the tubing being processed. Thus manufacturers have found it convenient to enlarge slightly the recommended TEMA tube sheet hole sizes to accommodate Alonized tubes. The following tube/hole size combinations have been found to be most convenient by many manufacturers:

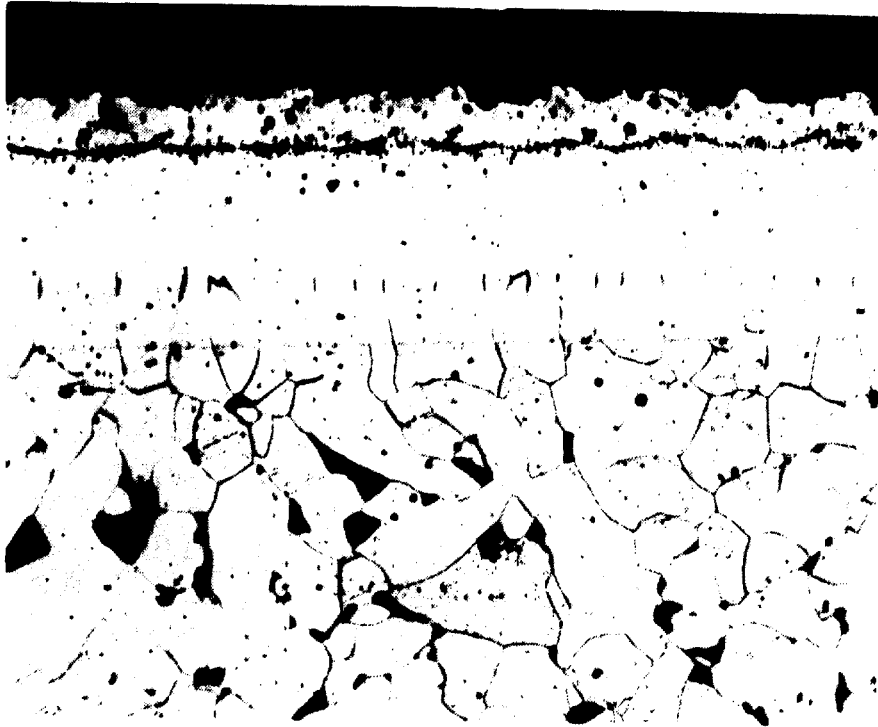
<u>Tube nominal O.D. before Alonizing</u>	<u>Tube sheet hole drilled size</u>
1" to 1-1/2" inclusive	Tube nominal O.D. before Alonizing plus .034"
Over 1-1/2" to under 2"	Tube nominal O.D. before Alonizing plus .036"
2" to under 2-1/2"	Tube nominal O.D. before Alonizing plus .038"
2-1/2" to under 3"	Tube nominal O.D. before Alonizing plus .040"
3" to 4" inclusive	Tube nominal O.D. before Alonizing plus .043"

All tolerance +.003" -.007"

These suggested combinations are made based upon the assumption that the tube sheet hole will not be grooved. If grooved holes are to be used, please contact Alon for their suggestions.

Figure 1

Alonized Carbon Steel
100 x
Nital Etched

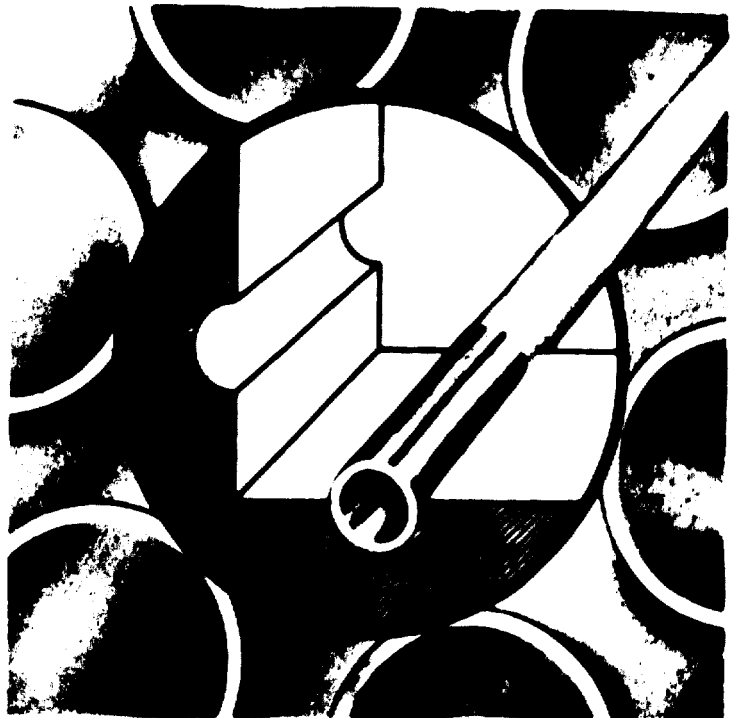


Diffusion Zone

Base Metal

Figure 2

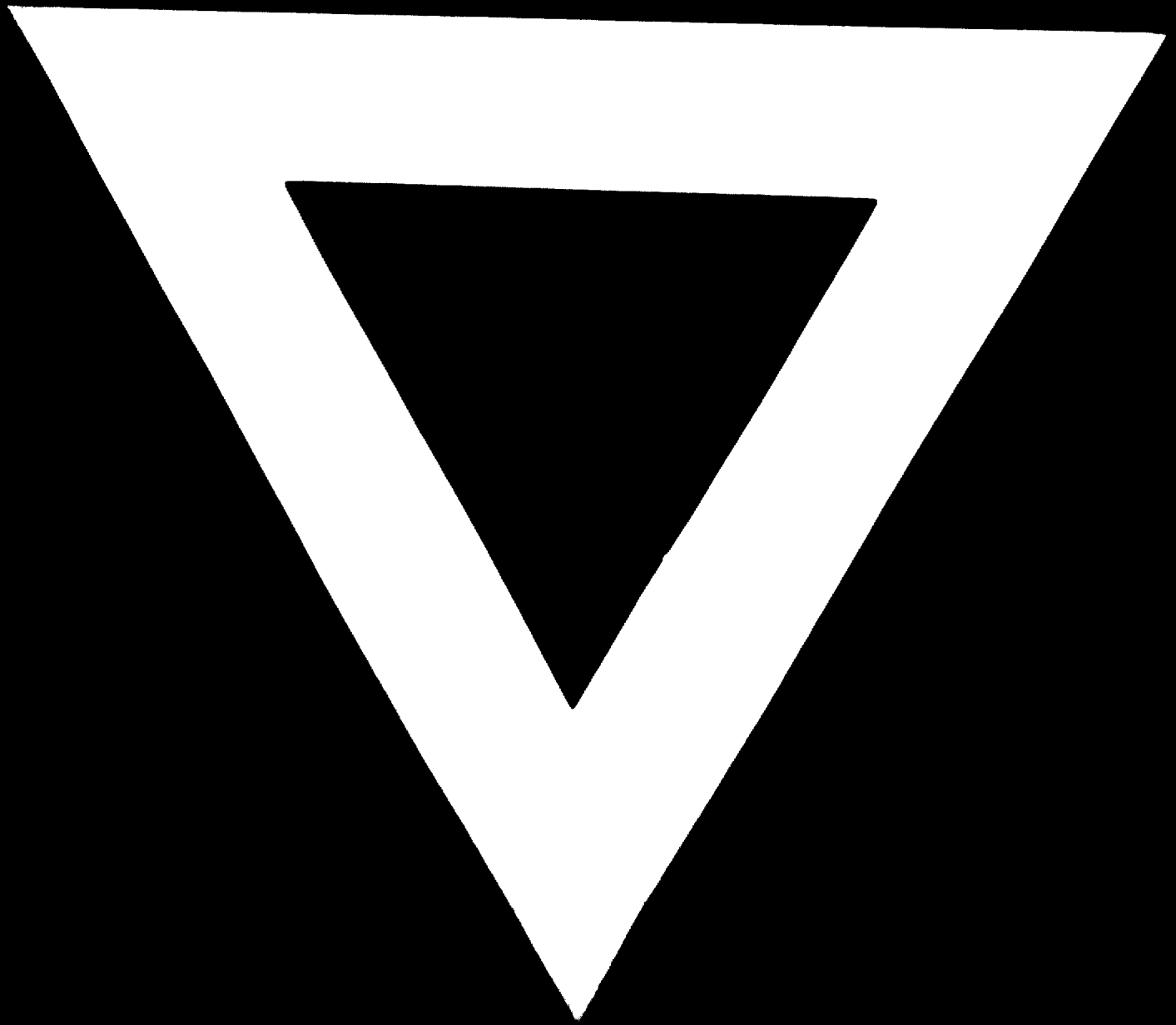
Cut away view of Alon-
ized tube ready for roll-
ing. Note unAlonized end
in contact with tubesheet.



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