

IMPORTANCE OF QUENCH BATH MAINTENANCE

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ABSTRACT

One of the primary purposes of any quenchant is to mediate heat transfer and enhance the surface uniformity throughout the quenching process. For polymer quenchants, this is achieved by the formation and subsequent breakage and removal of an insulating film surrounding the hot metal part upon initial immersion. To provide process control, it is necessary to minimize any changes in the uniformity of the heat transfer process caused by variation in polymer concentration, quenchant contamination, and polymer degradation. Therefore, an essential component of any well-run quenching operation is periodic monitoring of the quench bath. In this paper, procedures using inexpensive and easy to use equipment for maintaining a polymer quench bath will be discussed.

INTRODUCTION

Upon initial immersion of a heated part into a polymer quenchant, an insulating polymer film which controls heat transfer is formed around the hot metal as shown in Figure 1. The overall heat transfer mediating properties of this film are dependent on both film thickness (polymer concentration) and viscosity (polymer type and bath temperature) of the polymer used to formulate the quenchant. The timing of the film formation and subsequent rupture and removal is dependent on the film strength of the polymer, agitation (both direction and mass flow) and turbulence of the polymer solution surrounding the cooling metal.

There are numerous polymers that may be used in aqueous solution as polymer quenchants. The most commonly encountered polymers are: poly(alkylene glycol), poly(vinyl pyrrolidone), poly(sodium acrylate) and poly(ethyl oxazoline) [1]. Although this discussion will focus on quenchant maintenance procedures most often used for poly(alkylene glycol) -PAG quenchants, the procedures discussed are readily applicable to most of the other types of polymer quenchants. In this paper, various polymer quenchant maintenance concerns will be outlined. Recommended polymer quenchant bath maintenance tests, performance of these tests and interpretation

of test results will also be discussed. In addition, the effect of contamination on the uniformity of the polymer film surrounding the hot metal part during quenching will be discussed. Finally, some aspects of troubleshooting induction quenching problems will be described.

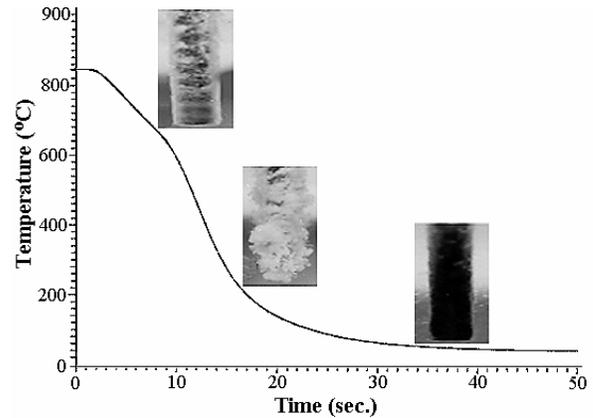


Figure 1 - Illustration of the quenching process for a PAG quenchant.

DISCUSSION

Polymer Quenchant Maintenance Concerns

A. Contamination

Optimal distortion control is achieved by maximizing the uniformity of the film formation and breakage at the metal interface during quenching. One of the most common causes of non-uniformity is quenchant contamination. For example, insoluble contaminants such as sludge deposits and oils, such as metal cutting and hydraulic oils, will result in non-uniform heat transfer due to the resulting film heterogeneity caused by oil droplets disrupting the otherwise "uniform" polymer film resulting in the creation of undesirable surface thermal gradients.

Oil contamination causes non-uniformity because oil droplets adhere to the surface of the hot metal surface interrupting the surface regularity of the polymer film. This will produce surface thermal gradients since the heat transfer rates through the oil droplet will be significantly different than the cooling rates through the adjacent polymer film. If the thermal gradients are sufficiently high, increased distortion or even cracking may result.

Foaming is another common problem that may be encountered in quenching. Foaming may be due to either chemical contamination or equipment design. Sources of chemical contamination include: detergents from cleaning solutions, metal working fluids, hydraulic fluids, even demulsified soluble oil antifoam compositions. Equipment design problems include undersized reservoirs, return lines entering above the liquid level, air leaks and pump cavitation.

As with oil contamination, foaming will lead to significant thermal gradients resulting in increased distortion or cracking. Instead of oil droplets, the non-uniformity is caused by the adherence of vapor bubbles to the metal surface.

Oils are perhaps the most easily detected contaminant since they form a distinct layer on top of the aqueous quenchant solution. Oils may be removed from the quenchant by skimming.

Other easily identified problems include carbon and sludge (from forging lubricants) contamination, metal scale which is identifiable by its magnetic properties and stable foam. Carbon and sludge may be removed by filtration or centrifugation.

It is much more difficult to directly detect soluble profoaming contaminants. It is easier to detect them by their profoaming behavior. Often this can be done by shaking the quenchant in a bottle and recording the relative foam breakage time compared to a "good" low foaming "control" solution. In some cases, foaming is best detected with a higher shearing process using a Waring blender set at high speed.

Foam problems are usually remedied by the addition of 50-300 ppm of an antifoam. Generally, a "cloud point" antifoam is preferred over the addition of a silicone antifoam.

Another source of soluble contamination is salts which may come from either quenching metals heated in salt pots (contamination through salt drag-out) or by the utilization of tap (or "city") water. Hard metal ions such as calcium, magnesium, and iron may build up in the system by evaporation and subsequent dilution processes. Increasing salt contamination produces accelerated cooling rates as shown in Table 1.

Salt removal may be facilitated by either a thermal separation process [5] or by reverse osmosis (RO) [6]. Thermal separation, which is only suitable for smaller quench systems, involves the heating of the aqueous-PAG quenchant solution above its separation temperature and then allowing the heterogeneous solution to settle. This process is depicted in Figure 2. Except for very high salt contamination levels where the density of the aqueous salt solution is greater than that of the

hydrated PAG polymer, the aqueous layer is the upper layer and is siphoned off. The remaining hydrated polymer is rediluted with distilled water, the corrosion inhibitor concentration is corrected at which point the quenchant solution is ready for reuse.

TABLE 1
EFFECT OF SALTS ON COOLING RATES¹

Salt Conc. (%) ²	Maximum Cooling Rate		Cooling Rate at 343°C (650°F)	
	(°F/s)	(°C/s)	(°F/s)	(°C/s)
0	70.2	39.0	45.5	25.3
3.0	97.2	54.0	57.2	31.8
6.0	118.4	65.8	63.0	35.0
Water ³	111.2	61.8	59.4	33.0

1. Data was obtained using a 25 x 50 mm (1 x 2 in.) cylindrical Type 304 stainless steel probe instrumented with a Type K thermocouple inserted at the geometric center. Agitation was provided by a radial flow at 23 L/min (6 gal/min) of the 20% of a TYPE I (AMS 3025) PAG polymer quenchant solution at 40°C (100°F) by the probe surface.

2. The salt was sodium nitrite.

3. Distilled water containing no polymer. The quenching conditions were the same as for (1).

Separation temperature		Water in separated PAG layer, %
°C	°F	
80	(175)	70
90	(195)	46

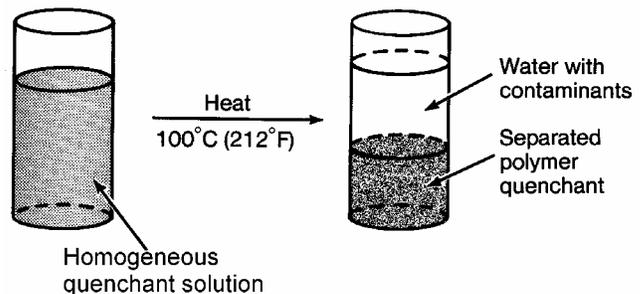


Figure 2 - Illustration of salt contaminant removal from an aqueous PAG polymer solution by thermal separation.

For larger quench tanks, the preferred method of salt contaminant removal is by reverse osmosis [6]. This process involves passing the salt contaminated aqueous quenchant solution through a semi-permeable membrane. The smaller salt ions and water will pass through the membrane and the polymer will not. After all of the salt is removed, the concentrated polymer solution is removed from the filtration unit by back flushing. The concentrated PAG polymer is rediluted, the corrosion inhibitor is readded and then the quenchant solution is ready for reuse.

Salt contaminants may be readily determined by measuring the conductance of the quenchant solution by dipping a probe into the quenchant solution. A typical instrument is illustrated in Figure 6. Salt contamination results in higher solution conductivity and may be due to hard metal ion build-up from tap-water used for redilution, salt drag-out from salt pots or corrosion due to corrosion inhibitor depletion.

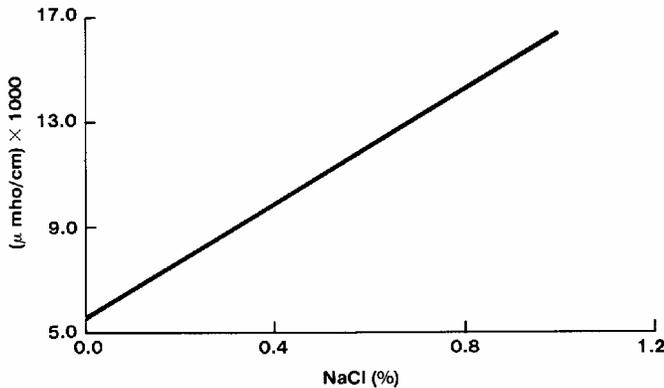


Figure 6 - Illustration of a conductance meter and the effect of

increasing salt contamination on conductance.

Polymer Concentration

As the figures of the cooling process above showed, heat transfer during quenching is controlled by both viscosity and thickness of the polymer film. The viscosity of the polymer is determined by the selection of the particular polymer used to formulate the quenchant. Thickness of the polymer film is controlled by concentration of the quenchant.

Polymer concentration may be monitored by the use of a hand-held refractometer shown in Figure 7 or by the use of a viscometer shown in Figure 8.

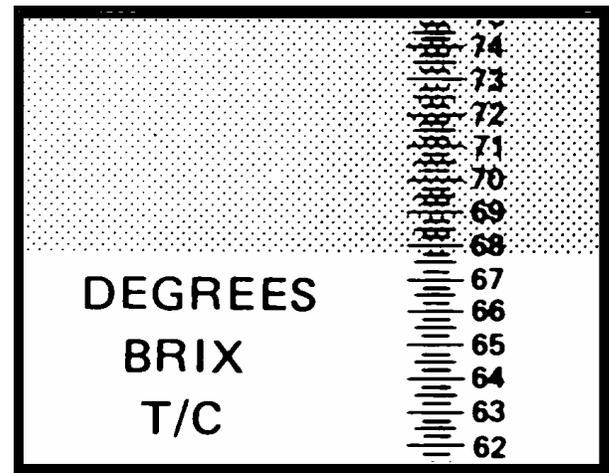
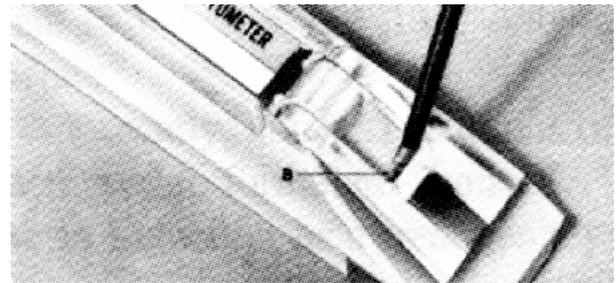


Figure 7 - Illustration of the use of a hand-held refractometer and the response of refractive index to varying quenchant concentration.

The use of a temperature-compensated hand-held refractometer as illustrated in Figure 7 is the most commonly used test for monitoring PAG quenchant concentration in the world today. Quenchant concentration and refractive index is linear relationship. However, refractive index is also significantly affected everything that may be present in the quenchant, including contaminants, often producing significant errors. Refractive index is not strongly affected by quenchant degradation. Therefore, it is not wise to rely solely on refractive index as the quenchant characterization method

without periodic validation by a different method.

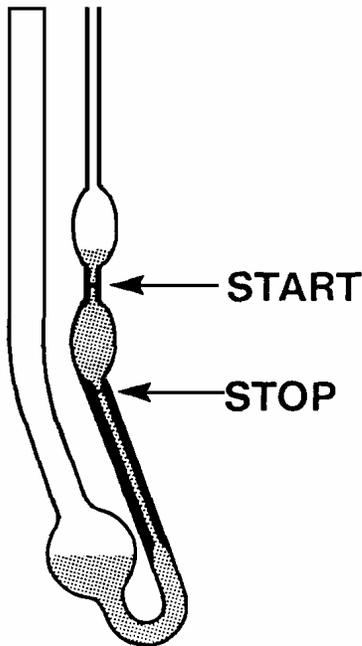


Figure 8 - Illustration of a Cannon-Fenske tube used to measure viscosity in conjunction with the necessary constant temperature bath and a viscosity concentration chart.

Viscosity is dependent on concentration and temperature and is readily determined using a Cannon-Fenske tube and a constant temperature bath as illustrated in Figure 8.

Although viscosity determination is an excellent indicator of polymer concentration it is strongly affected by polymer degradation. Viscosity of higher molecular weight polymers may also be strongly affected by contamination. However, the viscosity of PAG polymers is not usually strongly affected by contaminants.

For PAG quenchants, both viscosity and refractive index are dependent on polymer concentration. Refractive index is strongly affected by presence of contaminants and weakly affected by degradation. Conversely, viscosity is only weakly affected by the presence of contaminants and strongly affected by polymer degradation. Many PAG polymer quenchant suppliers have opted to determine quenchant concentration by both methods for comparison [4]. Often the differences in concentration by these two methods (Δ) is indicative of a problem that must be resolved by additional analysis. Delta values in excess of 8-10 or sudden changes in delta suggest that further characterization work must be done.

$$\Delta = C_n - C_h$$

Polymer concentration variation may occur by either drag-out or by evaporation. Polymer drag-out by adsorption of the quenchant on the metal surface upon part withdrawal from

the bath which always occurs, although at varying process-dependent rates, will result in a decrease of the polymer concentration in the solution. This will cause a decrease in film thickness and increase in cooling rates during the quench. Periodic polymer quenchant replenishment may be necessary to maintain a constant concentration.

Since polymer quenchants are aqueous solutions, they are subject to normal water evaporation processes. When this occurs, distilled water must be added back to the tank to maintain the correct polymer concentration.

Degradation

Polymer degradation which results in a reduction in the molecular weight (size) of the polymer may potentially occur by one of two processes. One is mechanodegradation [2] and the other is oxidative/thermal degradation [3]. Mechanodegradation may be encountered with the use of high (>50,000) molecular weight polymers in high agitation rate processes such as spray quenching. All polymers are subject to potential molecular weight loss by oxidative or thermal processes. The extensive increase in cooling rates due to the decrease of polymer viscosity by extensive oxidative degradation is illustrated in Figure 9.

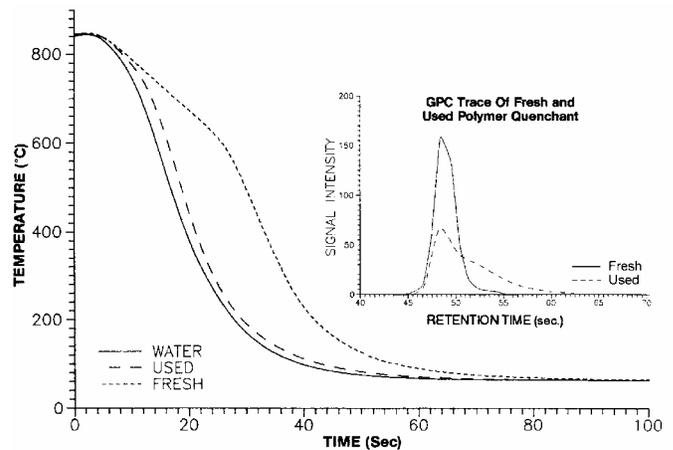


Figure 9 - Illustration of increasing cooling rates due to decreasing polymer viscosity from oxidative degradation.

Polymer degradation may be detected and quantified by a direct analysis of the change in the size of the polymer by a classical technique such as SEC (size exclusion chromatography). The use of SEC analysis to measure the change in polymer size due to degradation is illustrated in the inset of Figure 9.

Polymer degradation may also be detected by more classical and less expensive procedures. In the above discussion, it was shown that polymer viscosity is mostly

effected by polymer size. Thus the contributing effect of viscosity change to "delta" can be determined.

Separation temperature is determined by heating the quenchant and measuring the temperature where the fluid initially clouds out to the point where the thermometer is no longer visible. Although some salts may significantly affect the separation temperature [3], the most common variant is polymer degradation. Polymer degradation increases the separation temperature. It is not unusual for the separation temperature to increase approximately 2-4°C over the life of the bath. Larger increases or a sudden increase in separation temperature is cause for concern.

Polymer degradation may also occur by biological, usually anaerobic, processes. Such degradation processes are often caused by contamination by fluids such as coolants containing bacterial and/or fungal contaminants known as "bugs". The potential occurrence of biological degradation is minimized by daily agitation of the tank for at least 20-30 minutes. If bacterial contamination occurs, it may be treated with the addition of a bactericide or fungicide. Appropriate recommendations can be obtained from the quenchant supplier.

Corrosion Inhibitor

Since polymer quenchants contain water they must be used along with a corrosion inhibitor. All polymer quenchants should contain a corrosion inhibitor initially. Corrosion inhibitors provide protection to the tank and fixtures by one of two possible mechanisms: surface passivation or protective film formation. Either way, corrosion inhibitor depletions due to one of these mechanisms during normal use is to be expected. If adequate corrosion protection is to be maintained, periodic readditions to the quench tank are necessary.

Most, although not all, polymer quenchants contain sodium nitrite as the corrosion inhibitor. The concentration of sodium nitrite can be readily determined by a simple color test. In this test, a tablet which is available with the sample kit is dissolved in a known volume of the liquid and the resulting color is compared with the color of a known concentration of sodium nitrite on the color wheel as illustrated in Figure 10.



Figure 10 - Illustration of a portable calorimetric test for the presence of nitrite corrosion inhibitor.

Quenchant Troubleshooting Procedures

In addition to the bath maintenance procedures outlined above to monitor bath chemistry changes, there are a number of equipment design issues that should also be considered. These factors are:[7]

1. A closed and recirculating quench system should be used. The temperature controls for heating and cooling should be employed. It is critically important that heat be removed from the part at a properly controlled and reproducible rate.
2. The volume of the system should be a minimum of five times the maximum volume rate of flow that the quenchant is pumped per minute. For example, if the flow rate is 400 l/min, then the volume of the tank should be 2000 l.
3. The quenchant must be kept clean. Solid contamination not only produces non-uniform at the hot metal interface but it also plugs quench holes.
4. Low concentrations (~5%) of the quenchant minimize the potential for cracking by facilitating more uniform surface wetting than achievable with water itself.
5. If the hardness pattern extends into a shaft, cracking potential can be minimized by immersion quenching. If spray quenching is used, an auxiliary spray stream is required for the end face of the shaft. Non-uniform quenching will lead to quench cracking.
6. There are various causes of soft spotting and include:
 - a. The so-called *barber pole* effect is caused by a partial quench, usually a spray quench, followed by an interruption in cooling. The interruption may be due to a steam pocket caused by an entrapped quenchant. An illustration of the barber pole effect is shown in Figure 11.
 - b. Soft spotting may be caused by deflection of the quenchant caused by a change in the geometry of the part. An illustration of soft spotting is illustrated in Figure 12.
 - c. Splines in a shaft may act as paddles and throw off the quenchant during rotation leading to soft spots.
 - d. Shaft wobbling may lead to a spiral soft spotting pattern on a spray quenched rotating shaft. Shafts must be straight and centered in the inductor.

7. Pressure and orifice size recommendations for induction hardening with a polymer quenchant are provided in Table 2. [8,9]

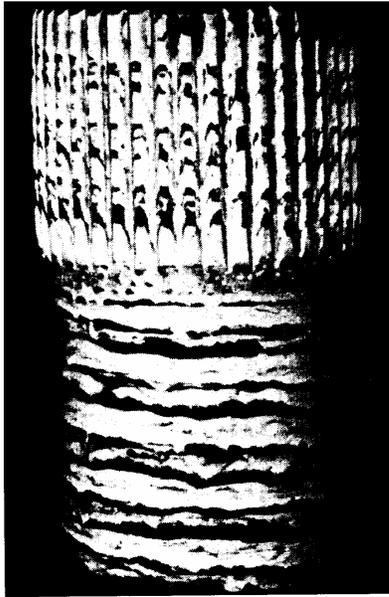


Figure 11 - Illustration of the "barber pole" effect.

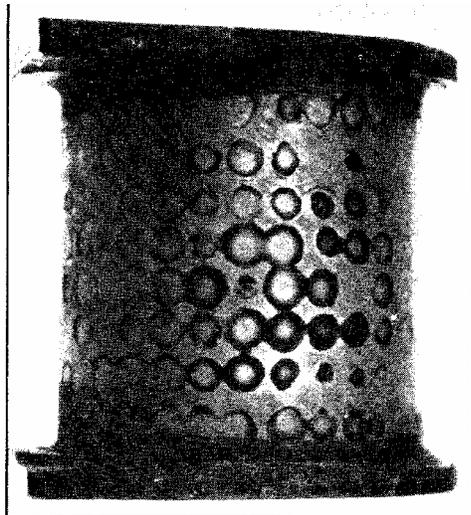


Figure 12 - Illustration of soft spotting.

in.	mm	in.	mm	(gpm/hole)
0.5	12.7	1/16	1.58	0.33
1.0	25.4	1/8	3.18	1.50

8. A correlation of recommended quench ring hole area, pressure and flow rate is provided in Figure 13. [8]

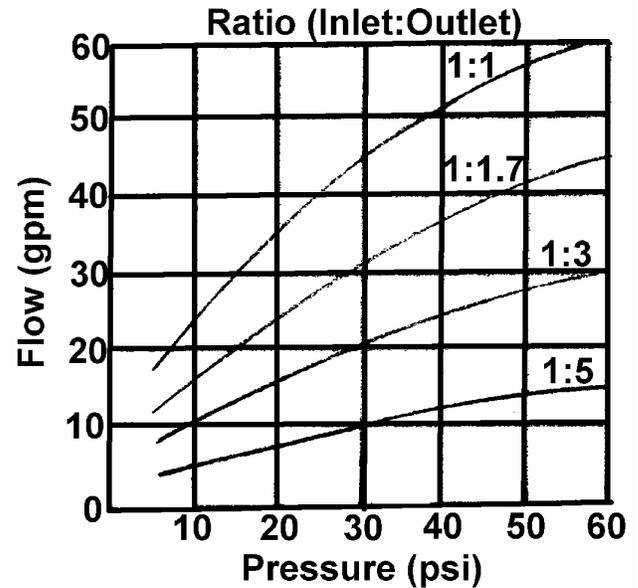


Figure 13 - Correlation of quench ring orifice size, flow rate and pressure.

CONCLUSIONS

A summary, description and strategy for use of various bath maintenance procedures suitable for use with quench tanks used for induction hardening applications have been provided. The deleterious effects of bath contaminants such as oil, foam and solids on quench uniformity have been illustrated. Some of the more significant quench system recommended design criteria were discussed. Proper attention to all of these factors will produce optimal quench results with the minimum of undesirable distortion and cracking.

REFERENCES

1. G.E. Totten, "Polymer Quenchants: The Basics", *Adv. Mater. Proc.*, 1990, Vol. 137 (No.3), p. 51-53.
2. L.S. Zharkin, S.V. Sheberstov, N.V. Panfilovich, and L.I. Manevich, "Mechanodegradation of Polymers. The Method of

TABLE 2		
INTERRELATIONSHIP BETWEEN HOLE CROSS SECTION AND FLOW RATE		
Cross Section	Hole Diameter	Flow Rate at 20 psi

Molecular Dynamics", *Russ. Chem. Rev.*, **1989**, Vol. 58 (No. 4), p. 381-392.

3. G.E. Totten, C.E. Bates and N.A. Clinton, ***Handbook of Quenchants and Quenching Technology***, ASM International, 1993.

4. E.R. Mueller, "Polyglycol Quenchant Cleanliness: Are There Benefits?", *Heat Treating*, **1983**, October, p 24-27.

5. L.M. Jarvis, R.R. Blackwood, and G.E. Totten, "Thermal Separation of Polymer Quenchants for More Efficient Heat Treatments", *Ind. Heat.*, **1989**, November, p 23-24.

6. R.D. Howard and G.E. Totten, "Membrane Separation of Polymer Quenchants", *Metal Heat Treat.*, **1994**, Sept./Oct., p. 23-25.

7. O.S. Sparks, "Important Factors in Quenching Systems for Induction Hardening", Preprint available from Tenaxol, Inc., 5801 W. National Ave., Milwaukee, WI 53214.

8. D.J. Williams, "Quench Systems for Induction Hardening", **1995**, July/August, p. 33-37.

9. G.E. Totten, G.R. Garsombke, D. Pye and R.W. Reynoldson, "Heat Treating Equipment", in ***Steel Heat Treatment Handbook***, Ed. G.E. Totten and M.A.H. Howes, Marcel Dekker Inc., New York, 1997, p. 448-452.