

Surface Treatment Of Polyolefins For Decorating And Adhesive Bonding

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Plastics Service Center, Bartlesville, OK

Polyethylene and polypropylene have chemically inert and non-polar surfaces. Surface treatment of polyethylene and polypropylene is required for acceptable adhesion of decorations, coatings and adhesives.

Oxidation of polyolefin surfaces may be performed by **flame, chemical or electronic methods** to produce a receptive polar surface. Polyolefin resins may be decorated by any of the known methods of decorating plastic. Adhesive bonding may be accomplished by any adhesive which will "wet" a polar polyolefin surface.

This paper will help you determine when and how to apply flame treatment for proper adhesion of decorations, coatings, and adhesives.

All three methods of surface treatment listed above are effective when properly used. Each is designed for particular applications and has stringent limits. The following comments are offered as a guide for the surface treatment of specific fabrication methods:

Film The electrical method is the preferred approach. Electrical treating equipment is inexpensive, clean and easily adapted to inline operations. The low amount of heat associated with electrical treatment is the primary reason for its preference over the flame method. The flame technique may be used but it is considerably more difficult.

Sheet The electrical method is not normally associated with treatment of sheet because of the thickness limitations of corona discharge treatment. Approximately 25 mils is the maximum thickness of sheet that can be treated by the electrical method. For most sheet applications, the flame method is preferred. Occasionally, confusion arises over whether or not the thermo-forming process provides sufficient surface oxidation to maintain adhesion of printing inks. Not only does thermoforming not provide any treatment, but it will remove any surface oxidation or treatment performed prior to forming. For thin wall thermoforms, warpage may be avoided by increasing the conveyor speed, moving the part further away from the flame tips or reducing the BTU output of the burner. All three separate, or any combination, will reduce the treatment level, so that care must be exercised to keep the level of treatment high enough for proper adhesion.



Injection Molded Products Flame treatment is normally used because of the thickness, size and shape of the parts. Avoid placing excess heat in the part which may relieve molded-in stresses and bring out flow marks. These same comments apply to thermoforming. Excess heat will also remove the gloss from a part. Sometimes this is objectionable and can be prevented as stated above. The Appendix covers the requirements and parameters of flame treatment in detail.

Blow Molded Products Again, because of the wall thickness and shape of the parts, the flame method is generally used. In the case of bottles or other blow molded items which have a matte finish, the flame does not present the problem of maintaining a glossy surface. Bottles may also be treated by the suppressed spark method. This method is effective and relatively easy to use. The suppressed spark method treats the entire surface of the part so that no registration or alignment of the part to the treater is required. Parts may be placed at random on the conveyor system. The lone drawback to the suppressed spark method is the equipment cost.

Rotational Molded Products The same comments apply as discussed for treating blow molded or injection molded products. Chemical treatment is normally reserved for applications that require the entire surface of the part to be treated. Chromic acid does provide a very good treatment, but the acid weakens and must be changed periodically. The system is hazardous and is not recommended unless proper handling facilities are available for the acid. Vacuum metallizing and dip coating operations normally will use this method.

With proper equipment, a good lasting treatment may be achieved without undue difficulties. Properly stored parts will retain the surface treatment for a minimum of one year. Care should be taken to avoid contaminating the parts prior to treatment. Contaminants will hinder the treatment except where the chemical method is used. The acid cleans the part prior to treating. Following are some contaminants which will reduce the treatment.

Additives High concentrations of slip, antiblock and antistats can adversely affect the level of treatment. Additive blooming can be counteracted by early treatment and decorating after processing.

Handling Areas handled with oily hands will not treat. Use clean white gloves to handle parts.

Machine Oil and Grease Keep parts away from dirty equipment. Grease and oil spots will not treat.

Mold Releases No mold releases should be allowed regardless of the advertising claims by the manufacturer.

Along with attaining good surface treatment, care should be taken to retain the treatment because surface treatment is easily removed. Since neither presence nor absence of treatment is noticeable to the naked eye, it is essential to avoid circumstances that would remove the treatment. To maintain good quality control avoid the following:

Excess Handling White, clean gloves should be worn by all personnel handling the treated parts. Oily hands remove treatment. Under no circumstances should the area to be decorated be handled.

Wiping the Parts Wiping treated areas with paper or cloth towels will remove the treatment. Dust or dirt should be blown off or rinsed with water and allowed to air dry. Keep parts free from dusty, dirty areas.

Since surface treatment is invisible, a good quality control method of testing the treatment is a must. The best test method to determine whether an ink or adhesive will or will not stick to the treated surface is to print or adhere a few samples, and test the samples with the Cross-Hatch Adhesion Test, or as it is sometimes called, "The Scotch Tape Test". Be sure the ink or adhesive has thoroughly cured before testing. Check manufacturer's recommendations for proper curing procedures. Discussion of decorating polyolefins is best when directed to a specific application and is beyond the scope of this TSM. Should additional advice be required for any type of decorating, please contact your nearest Phillips Sales Representative or the Sales Service Laboratory in Bartlesville, Oklahoma.



Effect Of Air/Gas Ratio On Treatment Level

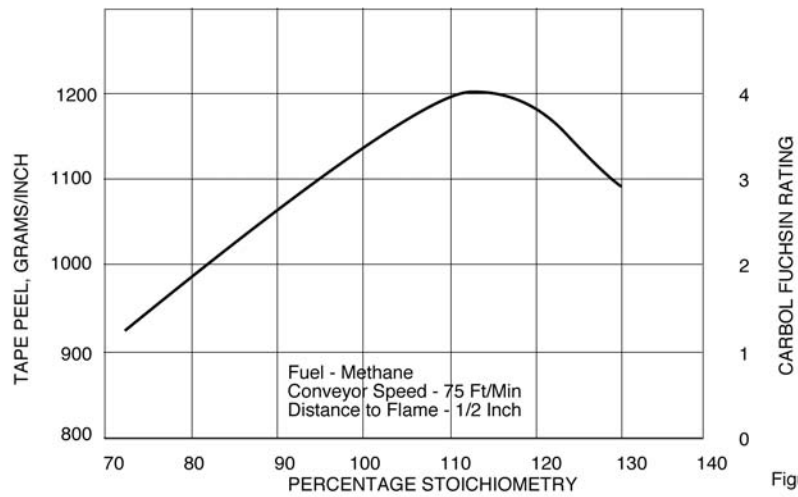


Figure 1

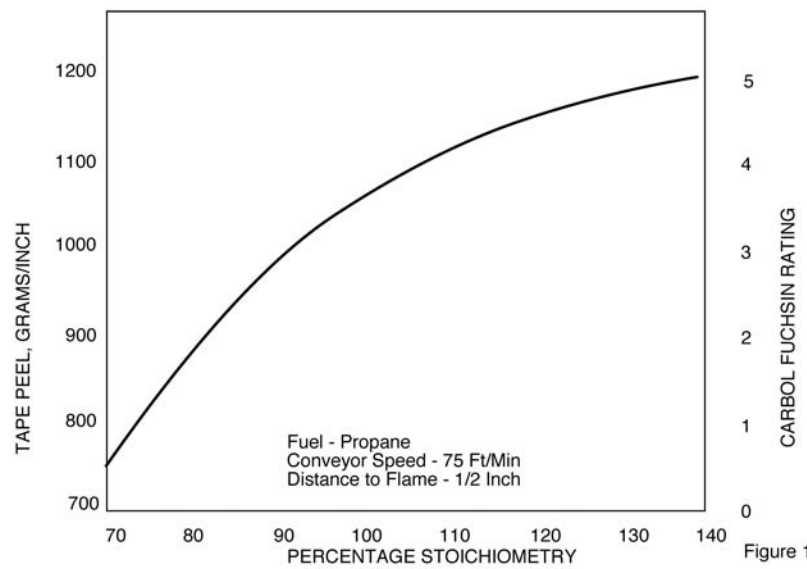


Figure 1A

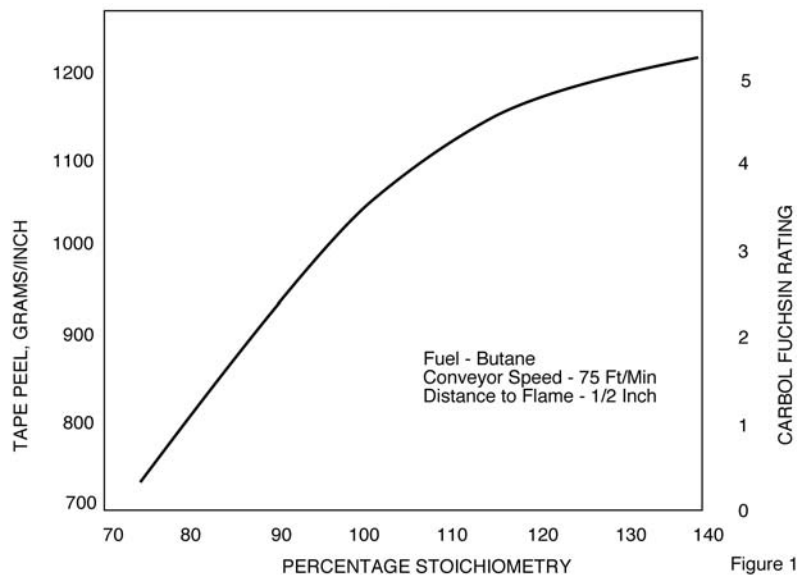


Figure 1B

APPENDIX

Flame Treating

Flame treating is one method whereby the surface of polyolefins may be made polar through oxidation. The exact mechanism of this reaction is not known. (Later research has led to the conclusion that the heat of the reaction serves as a catalyst, and that a chemical change takes place caused by the free reactive elements in the flame's active zone and the substrate. The basis for surface treatment success is the combustion reaction of a hydrocarbon gas. During the formation of the flame, free radicals are generated that penetrate the material being treated, thus modifying its surface wettability to achieve the optimum dyne level.) Although many theories have been advanced, the mechanism is not essential to this treating method. The treatment by an oxidizing flame is accomplished by operating within the parameters of three main variables involved in this method. The closer to optimum each variable can be set, the higher the resulting treatment level.

Any part of reasonable size or shape may be treated. The primary consideration will be the uniformity with which the flame will contact the area to be treated. The surface should not vary in distance from the burner more than one inch. In the case of cylindrical parts, they may either be rotated through a straight burner flame or dropped through a ring burner.

The surface to be treated must be free from dust, moisture, grease, mold release agents or any other foreign contaminants. Under no circumstances should the area to be treated be touched, handled or contaminated before or after treatment.

Apparatus

Gas Flow Meter Capable of delivering a required volume of gas to achieve BTU rating of burners.

Air Flow Meter Capable of delivering at least 15% greater volume of air than required for combustion of gas.

Air-Gas Mixer Venturi type, capable of mixing total volumes of air and gas.

Calibration Flow Curves Required for both air and gas flow meters. Flow rates should be given in SCFH or SCFM at standard conditions of 14.7 psia and 70° F for air (specific gravity of 1).



Apparatus, Continued

Air Regulator Capable of reducing from plant pressure to a constant 25 psig. Size to permit required air flow with no restriction.

Gas Regulator Capable of reducing pressure to a constant 0.25 psig to 1.0 psig. Size to permit required gas flow with no restriction.

Air Pressure Gauge 0 to 50 psi range.

Gas Pressure Gauge 0 to 1 psi to 5 psi range.

Needle Valves Required on air and gas mixer to closely control flow rates.

Burner Designed to give adequate flame pattern for treating.

Conveying Method To move the part through the flame at a constant rate of speed. Provision should be made to allow rapid adjustment of speed of the conveyor such as a variable speed drive or adjustable incline platform. Provisions for proper alignment and support of part are required.

Provisions for Adjustment of the distance between the burner and the part.

Standardization And Calibration Of Equipment

For the flame treating system to function properly, the equipment must be properly sized and installed in a specified manner. Various factors must be calculated to insure maximum efficiency of the system.

Sizing the flow meters: The flow meter sizes will be determined by the BTU/hr. rating of the burner or burners being used. The heat of combustion of the fuel gas being used will set the maximum flow rates of the meters. The heat of combustion of the common fuel gases are:

Methane (city gas)1000 BTU/SCF

Propane2500 BTU/SCF

Butane3100 BTU/SCF

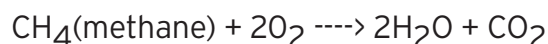
If a burner is rated at 30,000 BTU/hr., it will require 30 SCFH of methane, 12 SCFH of propane or 9.68 SCFH of butane. The gas flow meter will then be sized to permit these values to be the maximum flow rate. A sizing correction factor must also be used and is discussed in detail later in this TSM.

The air flow meter is then sized according to the maximum gas flow rate by the following method:

Maximum flow rate of air = Maximum flow rate of gas x amount of air required for combustion x sizing correction factor (10 CF Air/1000 BTUs of gas to the burner).

Calculation of the Stoichiometry of the Gas

All hydrocarbon gases combine with oxygen to produce heat in the following manner:



The prior equation indicates complete combustion of the fuel gas methane. The problem is how much air is required to complete this combustion for a given volume of any hydrocarbon gas. The following equation can be used to determine this value:

Equation 1

$$V = \frac{(A \times \% \text{CH}_4) + (B \times \% \text{C}_2\text{H}_6) + (C \times \% \text{C}_3\text{H}_8) + (D \times \% \text{C}_4\text{H}_{10}) + (E \times \% \text{H}_2 + \text{CO})}{100}$$

V = volumes of air required to complete combustion for 1 volume of gas.

A = 9.56 = volumes air required to combust one volume CH₄.

B = 16.7 = volumes air required to combust one volume C₂H₆.

C = 23.8 = volumes air required to combust one volume C₃H₈.

D = 31.0 = volumes air required to combust one volume C₄H₁₀.

E = 2.40 = volumes air required to combust one volume H₂ and CO.

If any of the above components are not present in the mixture, equate their volume percent to zero. Non-combustibles such as nitrogen and carbon dioxide are neglected.

The composition of the fuel gas may be obtained from the gas service company or from an analyst. The percent composition must be in volume percent. If the molar percent is given, it must be converted to volume percent.



Calculation of the Stoichiometry of the Gas, continued

All hydrocarbon gases combine with oxygen to produce heat in the following manner:

A fuel gas has the following composition by volume percent:

Methane (CH ₄).....	85.0%
Ethane (C ₂ H ₆).....	4.5%
Propane (C ₃ H ₈).....	2.1%
Butane (C ₄ H ₁₀).....	1.0%
Hydrogen (H ₂).....	2.0%
Carbon Monoxide (CO).....	0%
Nitrogen (N ₂).....	3.4%
Carbon Dioxide (CO ₂).....	1.4%
	<hr/> 100%

$$V = \frac{(9.56 \times 85) + (16.7 \times 4.5) + (23.8 \times 2.1) + (31.0 \times 1.6) + (2.4 \times 2.0)}{100}$$

V = 9.92 volumes of air required for complete combustion of one volume of gas.

This figure now represents 100% stoichiometric ratio. An addition of excess air will increase this ratio resulting in an oxidizing flame, whereas a decrease in air will decrease the ratio resulting in incomplete combustion.

Example: 15% excess air = 115% stoichiometric ratio = 11.41/1 air gas ratio for the above gas. A flame containing an excess of air is referred to as an oxidizing flame; a flame that does not have sufficient air to complete combustion is a reducing flame.

Sizing Correction Factor

The sizing factor compensates for the operating temperature, pressure and specific gravity of the gas versus the values used for calibration. Calibration values are 70° F, 14.7 psia and specific gravity of air (1.0).

The sizing factor is calculated as follows:

Equation 2

Sizing Factor - $\sqrt{\text{SpGr}_2/\text{SpGr}_1} \times T_2/T_1 \times P_1/P_2$

Where:

SpGr1 = specific gravity of air (1.0).

SpGr2 = specific gravity of gas to be metered.

(City gas = approx. 0.62, propane = 1.56, butane = 2.06).

T1 = 530°R or absolute 0 (460° R + 70 F = 530° R)

T2 = absolute operating temp. (+ 460 °R + operating temp.).

P1 = absolute pressure of one standard atmosphere - 14.7.

P2 = absolute operating pressure (14.7 + gauge reading).

This formula will yield the sizing factor to obtain the maximum equivalent air flow rate.

Example: Flow meters are required for a flame treating system that will produce 90,000 BTU/hr. The fuel gas is methane (1000 BTU/SCF) and has an air to gas ratio of 10.5/1. The average plant temperature is 90° F and four ounces (0.25 lb.) of gas pressure is available. The operating pressure for the air will be 25 psig.

Gas Sizing Factor = $\sqrt{0.62/1 \times 550/530 \times 14.7/14.95} = \sqrt{0.63} = 0.79$

Air Sizing Factor = $\sqrt{1/1 \times 550/530 \times 14.7/39.7} = \sqrt{0.384} = 0.61$

Thus, sizing factor x maximum metered gas flow (SCFM)= maximum air flow equivalent (SCFM).

In the example, 90 SCFH of methane will be required to produce 90,000 BTU/hr., or 90 SCFH/60 =1.5 SCFM of gas required. The 1.5 SCFM of gas flow must be converted to air flow for meter sizing. The conversion calculation is: Required SCFM of gas times gas sizing factor equals air flow equivalent (i.e. 1.5 x 0.79 = 1.19).

Since the air/gas ratio is 10.5/1, 10.5 more volumes air will be required than gas.

Thus, 10.5 x 1.5 = 15.75 SCFM of air will be required for 100% combustion. Since 15% excess air will be needed, the total required air flow will equal 15.75 x 1.15 =18.13 SCFM. Equivalent air flow will equal 18.13 SCFM x 0.61 (air sizing factor) = 11.06 SCFM. Therefore, meters with 1.19 SCFM and 11.06 SCFM maximum flow rates for air at 70°F and 14.7 psia would be required.

Correction Factor

The calibration curves obtained with the flow meters are for a given set of conditions, as mentioned earlier. The following correction factor formula is used to obtain the actual flow rates.



Equation 3

$$\text{Correction Factor} = \sqrt{\text{SpGr}_1/\text{SpGr}_2} \times P_2/P_1 \times T_1/T_2$$

The nomenclature is the same as for the sizing factor.

The value obtained from this equation is then multiplied by the flow rate of the calibration curve to obtain the exact flow rate in SCFM or SCFH.

Example: A flow meter is operating at 25 psig, 90° F with Butane (Sp.Gr. = 2.06). The calibration curve indicates flow to be 2.25 SCFM.

$$\text{Correction Factor} = \sqrt{1/2.06} \times 39.7/14.7 \times 530/550 = \sqrt{1.26} = 1.12$$

$$\text{Actual Flow} = 1.12 \times 2.25 = 2.52 \text{ SCFM.}$$

NOTE: Calibration values are given in either standard cubic feet per hour (SCFH) or standard cubic feet per minute (SCFM). Caution should be exercised to work with the same units.

Example: SCFH 60 = SCFM, SCFM x 60 = SCFH.

The flow meters, valves, gauges and pressure regulators must be installed as per the following schematic flow diagram.

Figure 1: Air To Gas Ratio

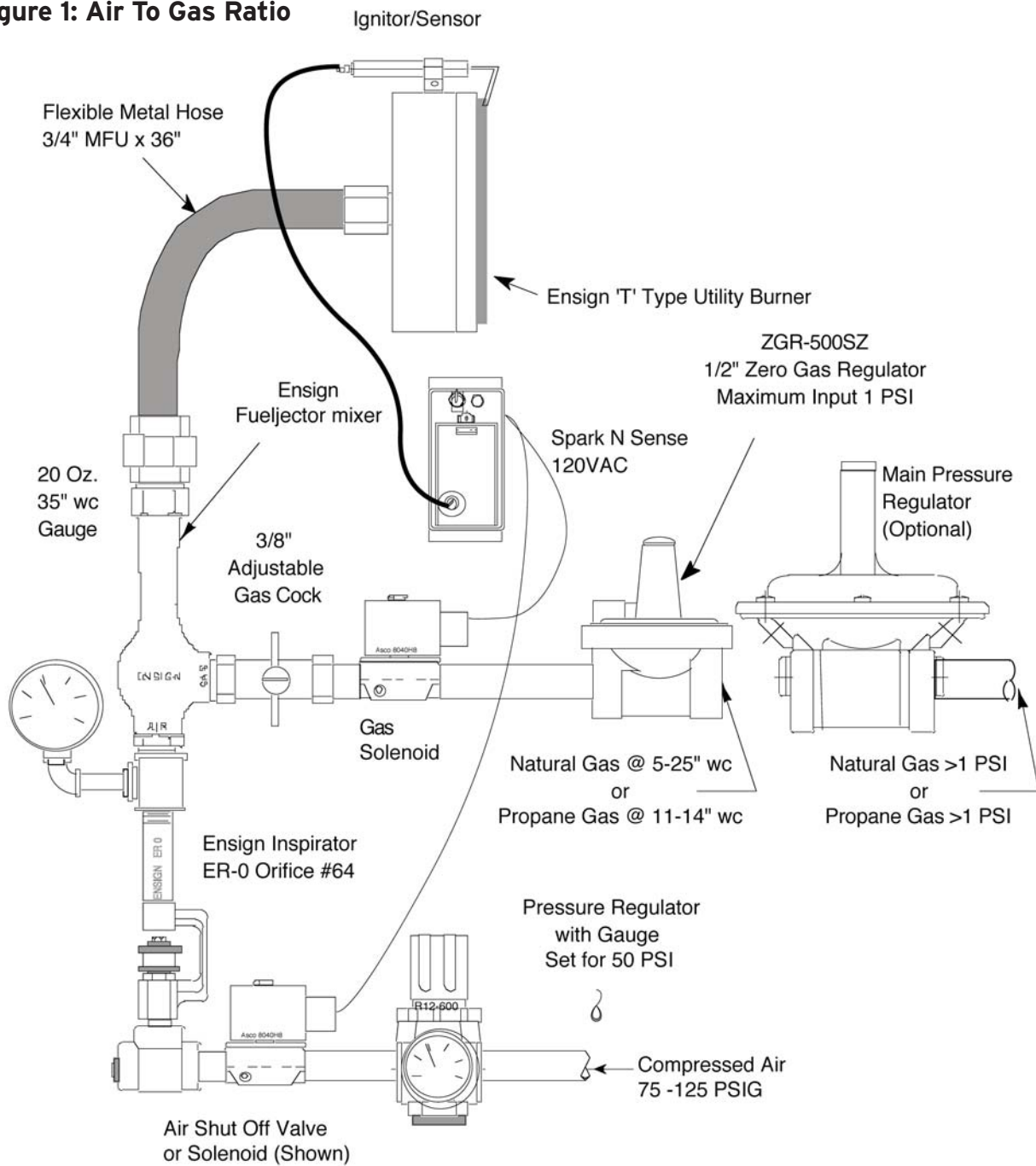


Figure 2: Treating Distance Of Flames

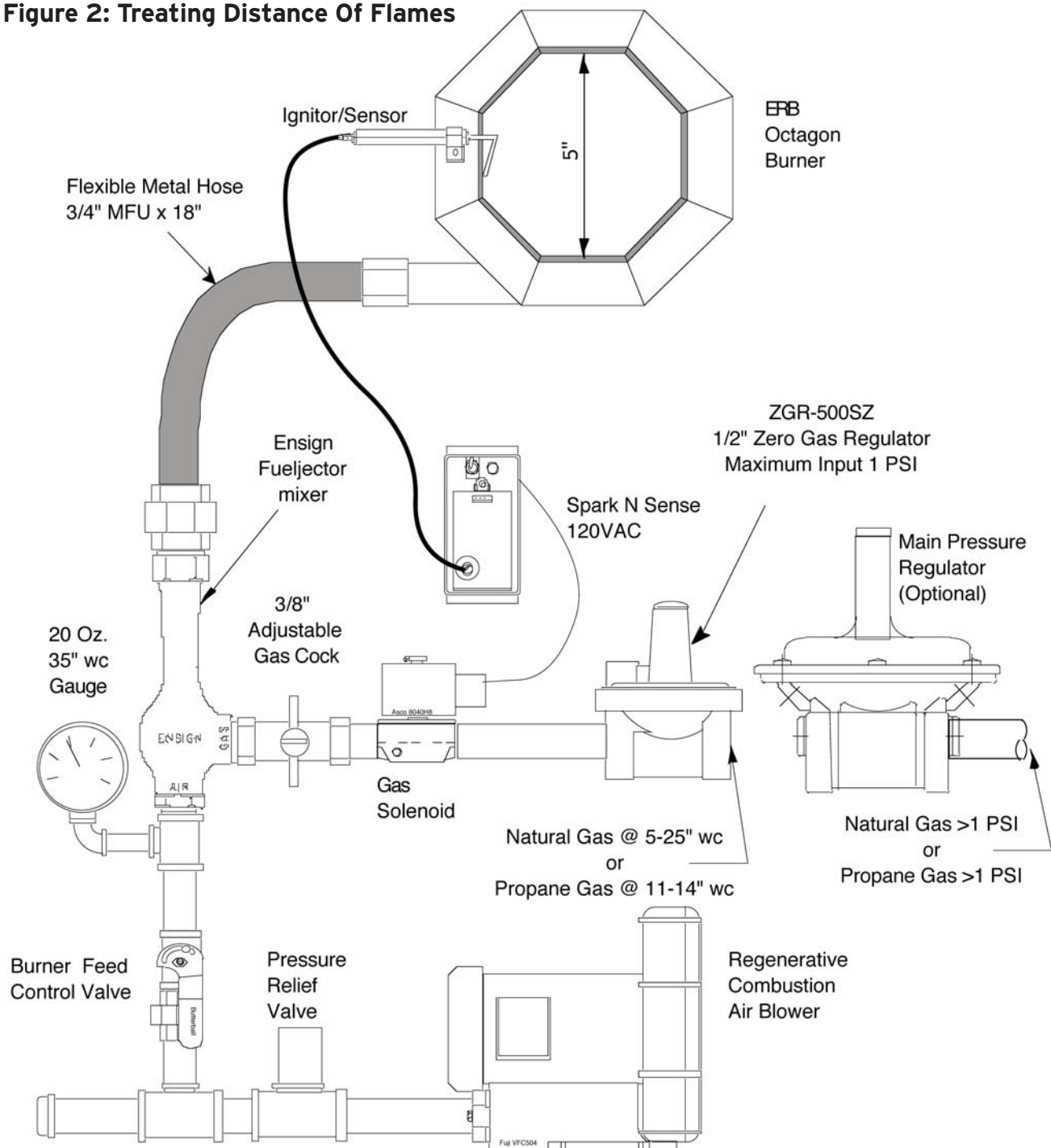
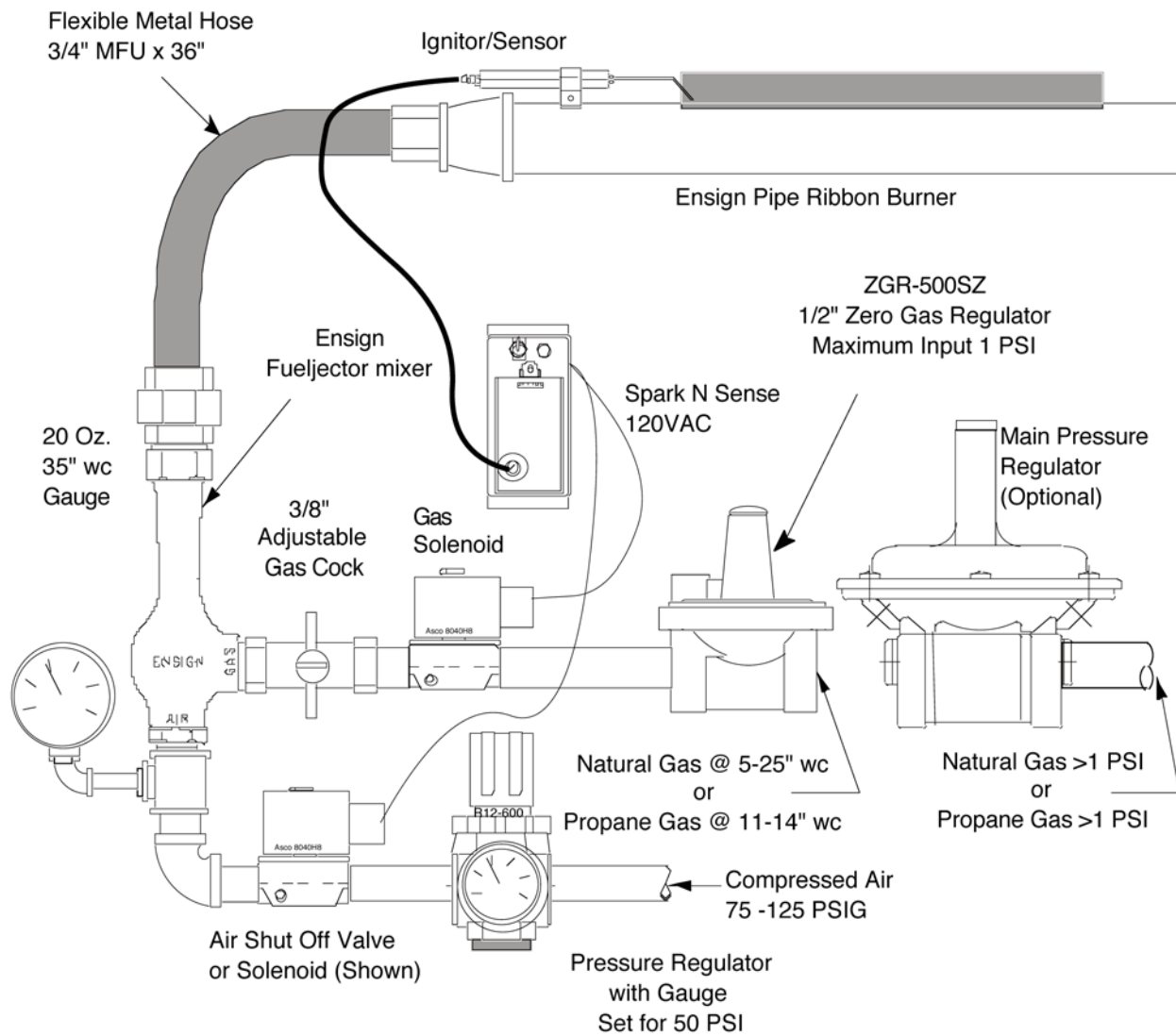


Figure 3: Contact Time Vs. Treatment Level



Procedure

1. Calculate gas flow to give required BTU output of burners. Use flow correction factor to find millimeters flow setting for the gas flow meter.
2. Calculate air to gas ratio.
3. Using air to gas ratio, calculate air flow required to obtain 110% stoichiometric ratio. Use correction factor to find millimeters flow setting for the air flow meter.
4. Set air and gas flows on values obtained and ignite burners. Ignition should occur only after the proper stoichiometric ratios have been attained. This will prevent a flash fire.
5. Set distance between visible blue tip of flame and surface to be treated at 1/2".
6. Start conveyor and set speed at 75 fpm (feet per minute).
7. Treat part and perform suitable surface treatment test.
8. If part did not treat, increase or decrease conveyor speed until treatment is obtained to a water wet level.
9. A slight adjustment may now be made in the air/gas ratio of the flame to obtain the optimum treatment. To determine optimum treatment, the water film in the water wet test should hold till evaporation.

Interpretations

Three main variables control the maximum treatment level. These variables are: 1) air to gas ratio; 2) distance of surface to be treated from visible blue tips of flame; and 3) speed with which part passes through flame. These variables may change slightly with resin type, BTU output of the burner or burner design.

1. Air to Gas Ratio The most critical of the three variables is the air to gas ratio, which must be closely controlled to achieve consistent flame treating. Air combusts with a hydrocarbon gas according to the following equation: $\text{CH}_4 \text{ (Methane)} + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$.

Equation 1 permitted the calculation of the volumes of air required to complete combustion of any hydrocarbon gas. A flame that has an excess amount of air is called an oxidizing flame and one that does not have enough air to complete combustion is called a reducing flame. A part may be treated only to the level that the flame is capable of producing in an optimized system regardless of the number of passes through the flame. Treatment level increasing with repeated passes indicates surface contamination being removed by flaming or excessive conveyor speeds. The effect of air to gas ratio is shown in Figure 1.

Normal operating values for the air to gas ratio will be in the range of 105 to 115% stoichiometric. The exact amount will depend on the gas being used and the resin type. This optimum value should be found by trial and error methods using a surface treatment test.

2. Distance of Surface From Flame Tips The optimum distance has been proven from numerous tests to be 3/8" to 1/2". It may not always be possible to achieve this exact distance over the entire area to be treated due to surface variation. In this event, 3/8" should be considered a minimum distance between the flame and the innermost surface to be treated. The actual treating portion of the flame extends approximately 1 1/2" beyond the flame tip, with 1/2" being capable of producing the highest level of treatment. The surface to be treated should never come in contact with the blue tip of the flame. This is the reducing zone of the flame and treatment will be greatly decreased. Figure 2 illustrates the treating distance of the flames.

3. Contact Time This variable must be closely controlled to achieve optimum treatment. Contact time is controlled by how fast the part is passed through the flame and depends on burner width, heat of combustion of gas, BTU output of the burner and resin type. The optimum speed must be determined by trial and error using the following guidelines:

- A. Set conveyor speed at 75'/minute and treat a part.
- B. If part is distorted or surface melting is observed, increase speed in increments of 10'/minute until acceptable treatment is accomplished.
- C. If no treatment is present and part is not dulled or excessively warm, pass part through flame again. If treatment is noted, slow conveyor down and repeat previous step. Continue to decrease speed until treatment is accomplished.
- D. Polypropylene requires a higher conveyor speed than polyethylene.
- E. If the BTU output of the burners is decreased by 50%, the conveyor speed must be increased by 50%. An exact amount of energy must be imparted to the surface to achieve treatment.

Figure 3 shows the relationship of contact time versus treatment level. With high density polyethylene, the BTU output of the burner was held constant at 30,000 BTU/hour and the distance of the flame tip to the part was 3/8". All three variables should be adjusted to optimum levels to attain the highest level of treatment possible. It will then be possible to properly store treated parts for extended periods of time with no significant decrease in treatment.



FUCHSIN DYE TEST

Significance

This test is primarily concerned with determining the degree to which the dye will stain a treated polyolefin surface. The dye is absorbed onto a treated surface and the color intensity produced is a measure of the surface treatment level. When applied as specified in the SPI Recommended Practice for Determining Level of Surface Treatment for Decoration of Polyethylene, the results can be used as part of production control or customer specifications. A relationship regarding the success with which a satisfactory decoration can be applied may be derived from the results.

Apparatus

1. Carbol Fuchsin Stain, Matheson, Coleman & Bell, CX390 or equivalent.
2. Distilled Water
3. Beaker
4. Disposable Gloves

Test Specimens

A treated polyolefin item regardless of size, weight or shape may be tested. No set number of specimens is required. Specimens with surface contaminants are to be avoided, for they may interfere with the color intensity produced by the test procedure.

Conditioning

Care should be taken that dust, dirt, grease, release agents or additives are not present or do not collect on the surface of the test specimens. Under no conditions should there be handling of the test area. Standard conditions are not a paramount consideration; however, tests should be performed under a reasonable temperature and humidity environment.

Procedure

1. Prepare the dye solution by dissolving one gram of carbol fuchsin in 100 ml of distilled water. Agitation will be required to insure that all particles of dye are in solution. The dye solution can be reused. Store in tightly closed container to prevent contamination.
2. Immerse the test area in the dye solution for four to six seconds.
3. Remove the test area from the dye solution and allow to drain in a vertical position for four to six seconds.
4. Flush test area with a gentle stream of tap water for 10-15 seconds to remove excess dye solution.
5. Allow test area to dry without wiping.

Interpretation

A. The dye solution is not light stable and grading the color intensity should be done immediately after test area is thoroughly dry.

B. The completeness of the correlation would depend on the object of testing. For example, in order to judge if a specific container has been treated sufficiently to accept a particular decoration, only one correlation is required. All test specimens equal to, or greater than, the standard in color intensity would be acceptable, while all less than the standard would be rejected.

C. The grading of color intensity is arbitrary; and consequently the test cannot be accurately correlated between laboratories.

D. A rating scale of 5 has been established using variable treatment levels:

0 - untreated

3 - Water wet level

5 - highest level

WATER WET TEST

Significance

This test is concerned with determining the degree to which a water film will adhere to a treated polyolefin surface. Water does not form a continuous film on an untreated polyolefin surface. Alteration of the surface by treating enhances the adhesion of a water film to some degree, relative to the level of treatment. When applied as specified in the SPI Recommended Practice for Determining Level of Surface Treatment for Decoration of Polyethylene, the results can be used as part of production control or customer specifications. A relationship regarding the success with which a satisfactory decoration can be applied may be derived from the results.

Test Specimens

Any treated polyolefin item, regardless of size, weight or shape, may be tested. No set number of specimens are required. The area to be tested should not contain surface imperfections which will mechanically aid in maintaining a water film.



Conditioning

Care should be taken that dust, dirt, grease, release agents or additives are not present or do not collect on the surface of test specimens. Under no condition should there be handling of the test area. Standard conditions are not a paramount consideration; however, tests should be performed under a reasonable temperature and humidity environment.

Procedure

1. Immerse the test area in distilled water for at least three seconds to wet the entire surface (Note 1). An alternate technique for large test areas is to flush the test area for at least three seconds.
2. Remove or cease flushing the test area, place test area in a vertical position, and observe the time that a continuous water film remains in the test area. Sixty seconds is a sufficient observation time.

NOTE 1: Water should be changed periodically to make sure that surface active agents do not contaminate the test water. The test water temperature should be between 65°F and 95°F.

Interpretation

- A. A film of water which breaks immediately is considered to be below the water wet level.
- B. A film of water which remains continuous for 5-10 seconds is considered to be water wet.
- C. The time the water film remains continuous is directly related to a treatment level above water wet.
- D. A continuous film may exhibit peripheral shrinkage and the speed of the shrinkage is dependent on the treatment level.
- E. Higher levels of treatment will maintain a continuous film of water until evaporation occurs.

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