Abstract # 44 Workshop - 10/13/2010 - 8:30 AM - Vine I & II
2 hours

Fuel Ratings Symposium 2010 "How to be Successful with CVCC"
Dr. Michael Croudace, Compass Instruments, Inc. - Jeff Bizub (DresserWaukesha), Nathan Pekoc (Compass Instruments, Inc.), Tom Bell (Exchange Group Data Services), Pat Ritz (PAC), and others
Compass Instruments, Inc.

This will be a users workshop in a panel discussion format. The topics covered will be applicable to all CVCC products sold and provide a DCN result. Users and manufacturers experts have been invited to participate on the panel. Topics which are scheduled to be discussed include but are not limited to: A) Importance of Combustion Air Quality, B) Fuel Issues like Handling, Filtering, Hysteresis, MCH, etc, C) Maintenance Activities, D) Interpreting Results, and E) Troubleshooting, etc. Fuel Ratings Symposium 2010 Workshop Presentation - 2 hours - 8:30 AM - Wed Abstract # 044

Questions and Summary of Answers for the Panel:

What are the main test variables that need to be controlled to produce accurate test results?

There were four main variables discussed that, if controlled, lead to accurate results

1. Accurate temperature control of the combustion chamber. This is taken care of automatically by each instrument manufacturer in their instruments and thus cannot be effected by the user.
2. Good calibration procedures. The user must follow good laboratory practices and follow the manufactures calibration procedures precisely. This means using a good source of air and purity of calibration fluids, which was discussed at length latter in the panel.
3. Accurate and repeatable fuel injection period so that exact and repeatable injection amount test fluids are injected into the combustion chamber. This is taken care of automatically by each instrument manufacturer in their instrument and thus cannot be affected by the user.
4. Good and repeatable quality air when running each test.

What are the main contaminants in air?

The percentage of oxygen, carbon dioxide and water content and most affect ignition delay times and thus DCN in any CVCC test.

How does air quality affect ignition delay?

Higher oxygen content shortens ignition delay times.
Water and Carbon Dioxide content reduces ignition delay times. Jeff Bizub showed a slide presentation (attached) which demonstrated the effects of water in your air source.

What air labels the customer should look for?

Zero Air, Synthetic Air or Breathing Air are all acceptable for use in CVCC tests. It is also a good idea to use 6 or more multipacks linked together to keep the air quality more consistent.

How do contaminants of calibration and validation chemicals affect results?

What are the contaminants?

The most common contaminants are peroxides which speed up ignition delay. Methyl Cyclohexane (MCH) easily forms peroxides. Inclusion of 10 to 15 PPM will affect ignition delay results.

Are their alternative chemicals?

Currently Primary Reference Fuel 98 is being evaluated as an alternative to MCH.

Are their ways to obtain or purify these chemicals?

The user should treat MCH with 13X molecular sieves in a column or by adding the sieves to the bottle of MCH. If the sieves are used to treat the MCH in the bottle it may take several treatments to remove the peroxides. Treat the MCH with sieves every time the user runs a test. The user should assume that MCH always contains peroxides.

What has been done to eliminate Hysteresis?

Hysteresis refers to the testing problem when a previous sample of fuel is not being completely evacuated from the instrument so that it affects the results of ensuing tests. Early testing showed that when fuels including high levels of cetane improver where tested prior to cetane improver free sample the cetane improver affected the next sample. Alternative flushing techniques for these early instruments have eliminated the problem.   Newer equipment designs also have eliminated this problem.

What is the referee method?

D -613. If there are disputes between DCN and D-613 results the user can use D3244 to resolve any differences.

CVCC Panel Discussion

Influences of Combustion Air and possible diluents of H20 and CO2

-JJ Bizub Dresser Waukesha

ASTM D7170/IP567 FIT Instrument

The following excerpts are bulleted points from the ASTM D02.01 meeting regarding the ASTM D7170 task force in December of 2007:

-It should be noted that the “tightening” of the air specification (which was done before the ASTM D7170 Interlaboratory Study, ILS, or round robin) was not done for O2% purposes. The O2 content affects only the Wall Temperature set-point to achieve calibration on normal heptane to achieve the required ignition delay value. (i.e. adjusting the wall temperature of the equipment can compensate for changes in O2 percent concentration when following the method’s guidelines)

-The air specification revision was done to ensure that tri-atomic molecules, or molecules of differing atomic mass are kept within acceptable limits. Tri-atomic molecules or molecules with larger atomic mass or less atomic mass are susceptible to ‘condense out of’ or ‘effuse from’ the air mixture at different rates than diatomic molecules per Graham’s Law of Diffusion (Effusion).

Real World Cases using different grades of Combustion Air:

Many different Choices, what is most common? What is important?

-Zero Air

- CEM (continuous emissions monitoring air)

- Synthetic or Primary Standard ‘air;

- Compressed air (cleaned of oils from compressor)

Real World Cases using different grades of Combustion Air:

Per ASTM D7170:

8.4 *Charge Air*—A compressed air containing 20.9 ± 1.0 volume percent oxygen (O_2), less than 0.5 PPM CO, less than 1.0 PPM CO_2, less than 5 PPM H_2O, less than 0.1 PPM NO_X, less than 0.1 PPM SO_2, and less than 0.1 PPM Total Hydrocarbon Content (THC). (**Warning—**Compressed gas under high pressure that supports combustion.)

NOTE 3—This grade air is typically referred to as Continuous Emissions Monitoring Grade Air (CEM).

Why was this chosen? What happens? Why does it happen?

Plausible Scientific explanation for an everyday occurrence

-Molecules “leave” the pressurized bottle at different rates

- Carbon Dioxide (CO_2) and Water or water vapor (H_2O) are diluents that “slow” the rate of combustion (rate of reaction)

- Having a controlled amount of the diatomic molecules found in standard air (Nitrogen N_2) and Oxygen (O_2) with small traces of other molecules will increase your time between calibration intervals, especially when you are a single bottle user of combustion air (using multiple bottles joined together on a manifold is another key to ensuring success and long time between calibration intervals).

Experiment: Using Heptane (calibration reagent) as a guide, let's track the ignition delays as the bottle of combustion air is consumed

Graham’s Law of Diffusion

Graham's law, also known as **Graham's law of effusion**, was formulated by Scottish physical chemist, Thomas Graham. Graham found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles. This formula can be written as:

$$\frac{\mathrm{Rate}_1}{\mathrm{Rate}_2} = \sqrt{\frac{M_2}{M_1}}$$

where:

$Rate_1$ is the rate of effusion of the first gas.

$Rate_2$ is the rate of effusion for the second gas.

M_1 is the molar mass of gas 1

M_2 is the molar mass of gas 2.

Graham's law states that the rate of diffusion of a gas is inversely proportional to the square root of its molecular weight. Thus, if the molecular weight of one gas is four times that of another, it would diffuse through a porous plug or escape through a small pinhole in a vessel at half the rate of the other. A complete theoretical explanation of Graham's law was provided years later by the kinetic theory of gases. Graham's law provides a basis for separating isotopes by diffusion — a method that came to play a crucial role in the development of the atomic bomb.

Graham's law is most accurate for molecular effusion which involves the movement of one gas at a time through a hole. It is only approximate for diffusion of one gas in another or in air, as these processes involve the movement of more than one gas.

Example

[e

Let gas 1 be H_2 and gas 2 be O_2.

$$\frac{\mathrm{Rate\ H_2}}{\mathrm{Rate\ O_2}} = \frac{\sqrt{32}}{\sqrt{2}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Therefore, hydrogen molecules effuse four times as fast as those of oxygen.

Graham's Law can also be used to find the approximate molecular weight of a gas if one gas is a known species, and if there is a specific ratio between the rates of two gases (such as in the previous example). The equation can be solved for either one of the molecular weights provided the subscripts are consistent.

$$M_2 = \frac{M_1 \mathrm{Rate}_1^2}{\mathrm{Rate}_2^2}$$

Periodic Table of Elements

- Alkali metals
- Alkaline earth metals
- Transition metals
- Lanthanoids
- Actinoids
- Poor metals
- Nonmetals
- Noble gases

- C Solid
- Hg Liquid
- H Gas
- Rf Unknown

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	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	1 H 1.0079	Atomic Sym Mass															
2	3 Li 6.941	4 Be 9.0121											5 B 10.811	6 C 12.010	7 N 14.006	8 O 15.999	9 F 18.998
3	11 Na 22.989	12 Mg 24.305											13 Al 26.981	14 Si 28.085	15 P 30.973	16 S 32.065	17 Cl 35.453
4	19 K 39.098	20 Ca 40.078	21 Sc 44.955	22 Ti 47.867	23 V 50.941	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.64	33 As 74.921	34 Se 78.96	35 Br 79.904
5	37 Rb 85.467	38 Sr 87.62	39 Y 88.905	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc (97.907)	44 Ru 101.07	45 Rh 102.90	46 Pd 106.42	47 Ag 107.86	48 Cd 112.41	49 In 114.81	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90
6	55 Cs 132.90	56 Ba 137.32	57–71	72 Hf 178.49	73 Ta 180.94	74 W 183.84	75 Re 186.20	76 Os 190.23	77 Ir 192.21	78 Pt 195.08	79 Au 196.96	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (208.98)	85 At (209.98)
7	87 Fr (223)	88 Ra (226)	89–103	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)	112 Uub (285)	113 Uut (284)	114 Uuq (289)	115 Uup (288)	116 Uuh (292)	117 Uus

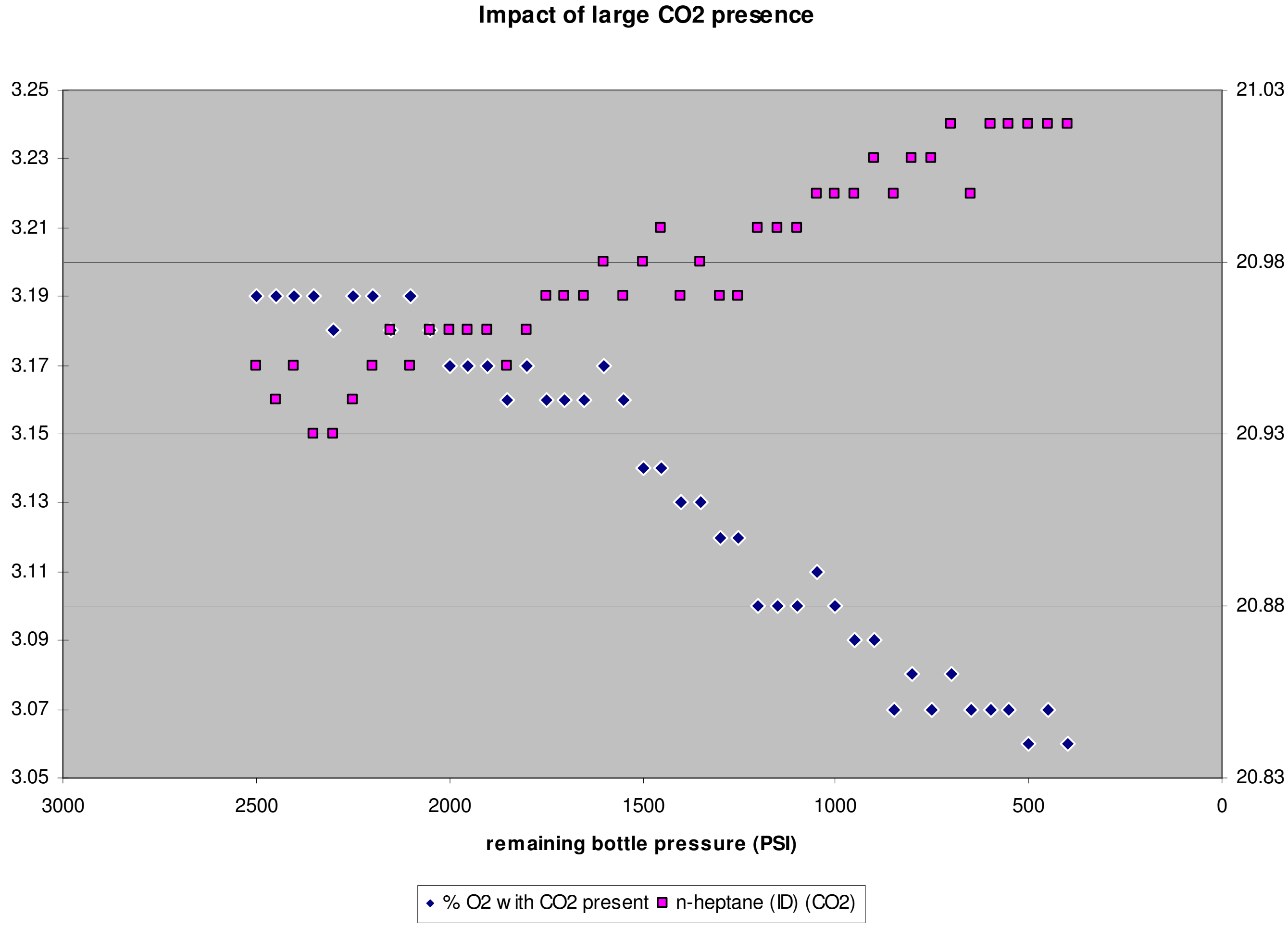
Example for Charge Air

- Atomic Weight of N = 14, for N_2 = 28
- Atomic Weight of O = 16, for O_2 = 32
- N_2 and O_2 will diffuse at similar rates
- Atomic Weight of C = 12
- Atomic Weight of CO_2 = 12 + 32 = 44
- CO_2 will diffuse at a slower rate than N_2 and O_2.
- Furthermore, CO_2 is an inert, and diluent that slows down combustion (it's widely used in Exhaust Gas Recirculation, EGR) as an inhibitor to prevent NO_x formations.

Similarly

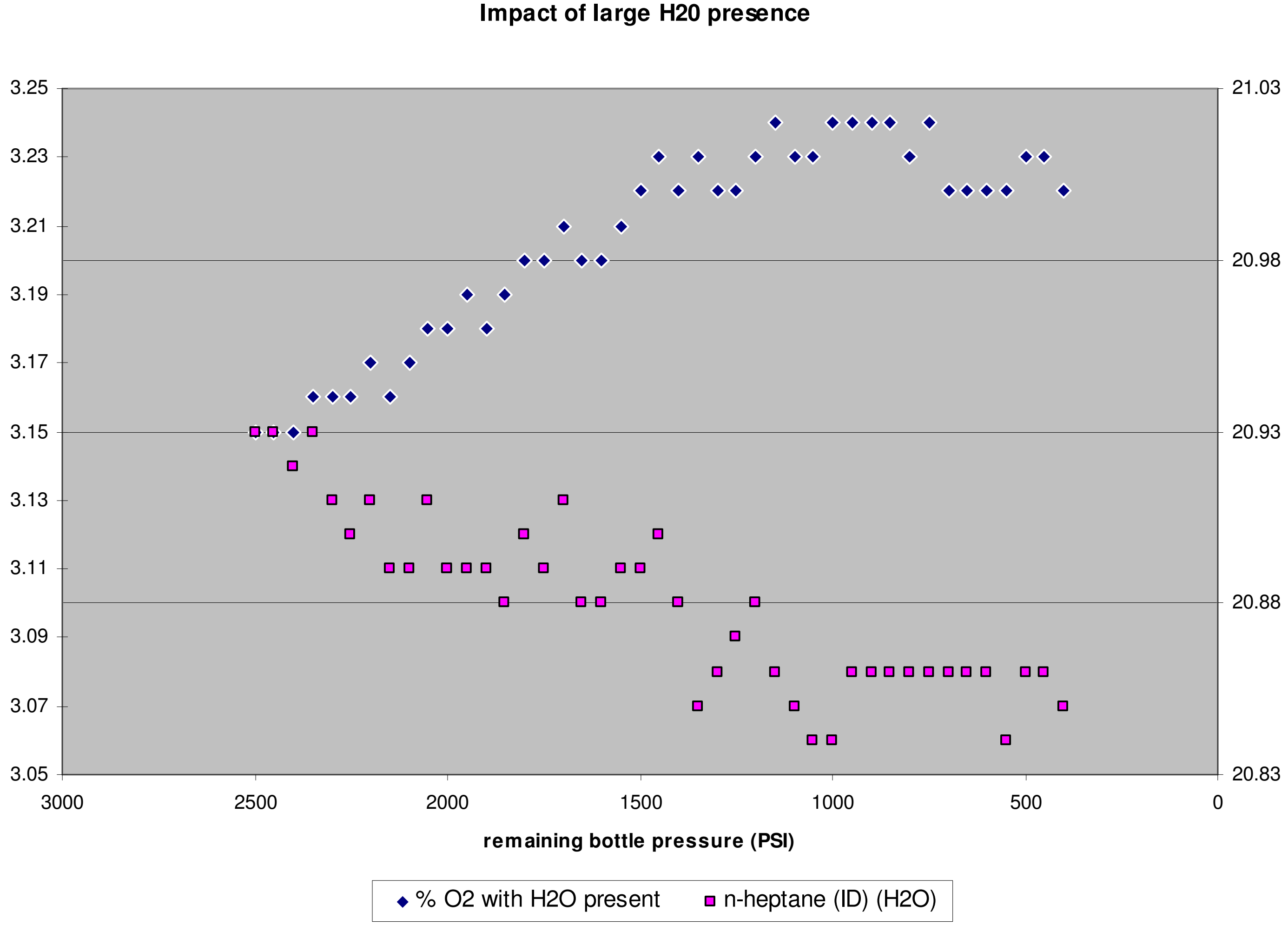
- Atomic Weight of N = 14, for N_2 = 28
- Atomic Weight of O = 16, for O_2 = 32
- N_2 and O_2 will diffuse at similar rates
- Atomic Weight of H = 1
- Atomic Weight of H_2O = 2 + 16 = 18
- H_2O will diffuse at a faster rate than N_2 and O_2.
- Furthermore, H_2O is also an inert and diluent, that slows down combustion (it's widely used in Exhaust Gas Recirculation, EGR) as an inhibitor to prevent knock (in water injection systems).

Impact of CO2



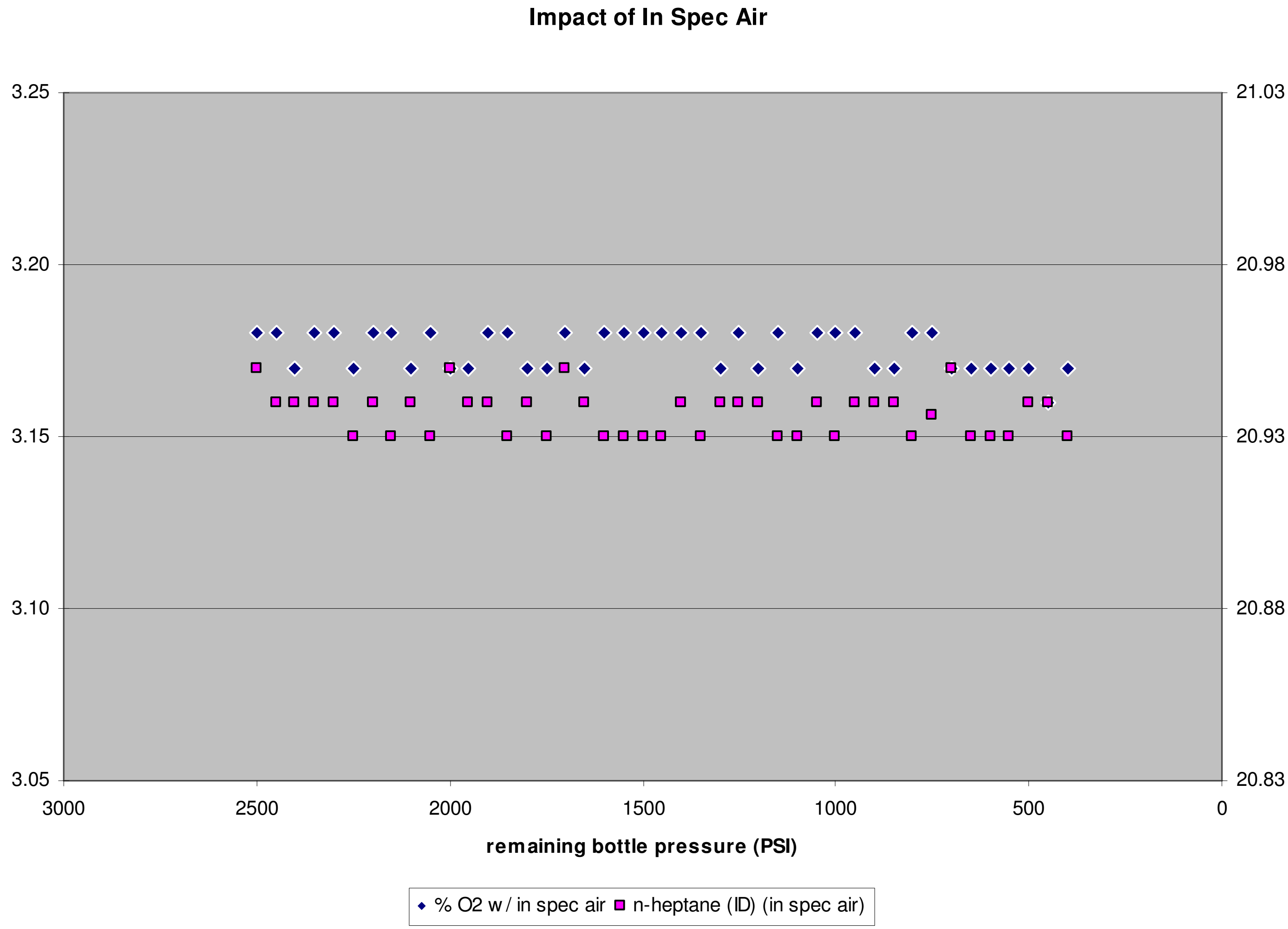
As bottle is depleted amount of CO2 left in the bottle goes up, O2 goes down and Ignition Delay gets longer (slower reaction) because of diluent effect

Impact of H20



As bottle is depleted amount of H20 left in the bottle goes down, O2 goes up and Ignition Delay gets shorter (faster reaction) because of diluents' effect is depleted

“In Spec” Air



As bottle is depleted we have a relatively constant O2 percent and constant Ignition Delay measurement (long term calibration stability)

In Summary

- The Charge Air Specification exists to avoid potential shifts in air bottle consistency as the air bottle is depleted. When pressure drops in the bottle (as the contents are consumed), the consistency of the remaining mixture may shift due to different diffusion/effusion rates.
- Users of the equipment that utilize bottle manifolds made up of more than 1 air cylinder will be less apt to seeing this shift in short times.
- The air specification was tightened to avoid this situation, particularly for those users that utilize only a single air cylinder for charge air.