

## Chapter VII. B

# Gas Permeation of Various Elastomers



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## PRODUCTION OF A RUBBER COMPOUND RESISTANT TO GAS PERMEATION ( UTILIZING TUBING PROTECTORS AS THE PRODUCT )

The following covers the work done to improve a special compound to be used for producing tubing protectors. Formulations previously utilized and designed for other applications. Opportunities arose for additional experimentation due to swelling and blistering of the finished product due to gas permeation. This was attributable to insufficient specifications and testing before the product was sent to the field.

After assembling of definite specifications and the securing of an adequate pressure reaction apparatus for high pressure gas testing, work was carried forward on a definite course to a successful conclusion.

### SUBJECT:

The object of this work was to design a rubber compound to withstand a gas pressure (ethylene) of 5000 psi at a temperature of 300<sup>o</sup>F. The product made from this compound must function well as a tubing protector and must process well enough to cause a low percentage of rejects during production

### SUMMARY

To find a compound from which to make tubing protector rubbers which will withstand 5000 psi gas (ethylene) pressure at a temperature of 300<sup>o</sup>F., many steps had to be taken. The search was to find the proper chemical ingredients and use them in the optimum amounts to give an easy processing stock as well. This was accomplished by thorough investigation of the constituents used in the compounds.

It was found that low Mooney (70-80) Nitrile would, when properly compounded and kept at a low volume percent, give a compound that would process excellently as well as maintain a high resistance to gas permeation. The best combination of plasticizers to use was found to be dioctyl-phthalate and dibutyl-phthalate at a 30 part (total) level.

The fine particle size fillers, such as Hydrated Silica and SAF Black, impart to the compound good physical properties while giving the best resistance to gas permeation. A near 50-50 loading of Silica and SAF Black gives a compound with a low mixed Mooney, which makes for easy processing. Thermal black, when added to the stock in addition to the other fillers, lowers the volume percent elastomer and aids greatly in improving processing.

A sulfur bearing chemical curing system proved to give the tightest vulcanization (cure) in the lab and also in plant production. A tight cure is necessary for the stock to have the highest resistance to gas permeation. An undercure will cause the compound to be severely attacked by the gas.

In the experimental compound all of the above was taken into consideration. The compound worked well in the lab and did not suffer in being put into production in the plant.

With extruded loads being used with the experimental formulation, it was the feeling (proven by lab tests) that tubing protectors can be recommended for operation in a well with bottom hole pressure

of at least 6000 psi at temperatures up to 300<sup>o</sup>F. From test results it was also felt that higher well temperatures, 300<sup>o</sup>-325<sup>o</sup>F. would not cause more gas permeation, but would, in fact, decrease the reaction.

#### PROCEDURE:

The gas permeation immersion tests were performed in a Paar type 4000 pressure reaction bomb. The gas used was dry ethylene from a standard bottle (1250 psi at start) and nitrogen in a standard bottle (2100 psi at start).

The samples for gas testing were compression set discs at first and changed to sleeves during the latter tests, and were prepared in the laboratory from lab mixed or factory mixed compound, and cured according to proper procedures for obtaining optimum physicals for each compound tested. Along with these samples, tensile sheets were prepared in order to test the physical properties of each compound developed.

In the case of the compression set discs, each was weighed before immersion in the gas chamber while the sleeves were installed on a piece of tubing, giving the same elongation as that obtained when actually installing tubing protectors for field use. The sleeves were then checked for length and O.D. before the gas test.

After the samples were put into the pressure apparatus, the apparatus was evacuated with nitrogen to be sure no air was left in the chamber. Next, the chamber was pressured to the maximum amount with ethylene alone or a combination of ethylene and nitrogen. It was found in the last stages of this test series, that higher pressures could be obtained by cooling the pressure apparatus to -50<sup>o</sup>F. overnight before each test, (This was due to the ethylene condensing out to the liquid stage and allowing a greater volume of ethylene to be charged to the chamber.) After the determined amount of pressure at room temperature was obtained, the pressure chamber was heated to the desired test temperature up to 300<sup>o</sup>F, which also increased the applied pressure.

The samples were kept in the pressure apparatus at the desired amount of temperature and pressure for a period of 72 hours, after which time they were taken out and reweighed or remeasured, as the case determined. The appearance was noted for each. All of the results were recorded and studied before proceeding to the next step.

#### DISCUSSION OF RESULTS:

This work covered a period of 5 months till completion and producing product for sale.

Tests #1 through #7 were used primarily to acquaint the laboratory personnel with the safest methods for operation of the pressure bomb and to determine the best conditions (temperature and pressure) for a starting point.

Tests #1 through #4 were made using standard plant formulations (compression set buttons) as those to be tested - 1) Neoprene; 2) High Acrylo-Nitrile; 3) Medium Acrylo-Nitrile; 4) Medium Acrylo-Nitrile; 5) High Acrylo-Nitrile; 6) Low Acrylo-Nitrile; and 7) Medium Acrylo-Nitrile. All of these tests were run at room temperature but the pressure was changed from 500 psi to 950 psi, to 1500 psi, to 2000 psi, respectively. It was determined from this four-test series that as the pressure increased, the swelling and blistering of the affected compounds increased to a severe point.

From the results obtained here, it was learned that the medium acrylo-nitrile was best toward low gas permeation and the neoprene and low acrylo-nitrile were the poorest. From these facts it was concluded that the neoprene polymer would never give a compound which would be resistant to ethylene gas permeation due to its high solubility in the gas. The gas actually dissolves through the polymer and is retained in the compound. It was also felt that low acrylo-nitrile content polymers would act similarly to neoprene, due to the poor results obtained with the low acrylo-nitrile formulation.

The next test series (Tests #5 through #7) were performed on the same formulations as those above. The only difference in procedure was to immerse the samples in ASTM #3 oil in the gas bomb before applying the gas pressure. Although the pressure was varied from 500 psi (Test #5) to 2000 psi (Tests #6 and #7) while room temperature was maintained, there was no damaging of the samples due to gas permeation. The ASTM #3 oil seemed to block the gas from entering the samples. This was probably due to the gas being absorbed into the oil and never reaching the surface of the samples. This could be the explanation of why there have been reports of tubing protectors in field installations not swelling on one joint while swelling and blistering severely on the next. Oil in the well could have blocked the permeation.

From the first seven tests we learned that the medium acrylonitrile was the best compound from production formulations for giving a gas permeation resistant product. From actual field use, it was known that this formulation would swell and blister severely and, on several occasions, had caused much trouble. The processing of this compound is also very poor and rejects run at a high rate. The job was then set out to: (1) Improve the processability of this formulation, (2) Improve resistance to gas permeation. These could only be accomplished by a comprehensive study of compounding. This was begun, starting with Test #8 - a study of plasticizers.

This test (#8) series produced results that indicated the Ester type plasticizers cause less gas entrapment or permeation than does the polymeric type. Reducing the plasticizer down to zero has definite beneficial advantages as far as resistance to permeation, but makes the compound very difficult to process. In this set up, the pressure was held at 950 psi and room temperature was maintained.

The next step (Test #9) was to investigate different types and levels of filler loadings. The thought here was to reduce the amount of Silica present or to add another filler which would tend to reduce the viscosity of the mixed compound and thus improve processing. Different combinations of blacks or clays and Silica were investigated. The addition or replacement with clay or FEF Black at the same filler loading level produced a degradation of resistance to gas permeation. A 10 vol. addition of Thermal black to the Silica loaded stock shows a marked improvement. Also investigated in this work was the incorporation of vinyl or polyethylene in the compound. Both produced worse gas resistance. During this work, the plasticizer (DOP) level was kept at 20 PHR. The main point learned from this testing was that a 75 PHR level of Silica was the datum plane. Any loading under this level produced poor gas resistance, any loading above improved gas resistance.

At this point it was decided to up the testing pressure to 1500 psi at 180°F. This was done to come more in line with conditions that would actually be found in field operation of finished tubing protectors.

With Test #10 three separate points of investigation were covered. The first being to

reevaluate the use of Liquid Acrylonitrile and DOP at various levels with added vulcanizing agent. The Silica level was kept at 75 PHR. The results indicated compounds with slightly better gas permeation resistance than the standard compound. The liquid nitrile in larger amounts exuded to the surface during the gas pressure test. The increased cure was added to be positive that the liquid nitrile did not rob from the cure and give an undercured piece. No advantage was seen in investigating the use of liquid nitrile further.

The second phase of this test was to investigate the replacement of Silica with Thermal and SAF Blacks. This was done while keeping the same plasticizer and filler levels as tried before. The substitution of thermal black caused the permeation resistance to become worse. The substitution of SAF Black had no harmful effect and actually seemed to improve the permeation resistance.

The third phase was to take the standard formulation, holding the Silica at the 75 PHR level and using only DOP as the plasticizer while changing to various polymers. Those tried were low nitrile, medium nitrile, and high nitrile from one supplier and low nitrile from another. The high acrylo-nitrile content of medium nitrile showed the best resistance in the gas test and was followed by the others in this order: Medium, Low, 1st; Medium (2nd); Low (2nd). It was felt that the two 2nd supplier nitriles gave poor results due to being undercured.

At this phase of the testing, the gas pressure was increased to 3000 psi at a temperature of 180°F.

Test #11 was primarily begun to recheck the various polymers used in test #10 but to increase the cure system where necessary so as to insure a good tight cure in the test samples. A carboxylated nitrile was included in this work. The added cure moved the medium nitrile (2nd) up in the class with medium nitrile (1st), and low nitrile (2nd) in a class with low nitrile (1st). The carboxylated nitrile gave the poorest results. Our point learned here is that to obtain equivalent cures of the 2nd supplier nitriles to the 1st suppliers nitriles, more cure must be added. For low gas permeation, a good tight cure is necessary.

Along with the above work, the use of Silicone LM-3 oil with Silica and replacement of one Silica with a different brand were run. This was a step to improve processing. Both systems proved to give poor compounds for withstanding gas permeation.

To find the best curing system for medium nitrile compounds using the same control formulations, Test #12 was made. From this work it was found that a sulfur, Santocure and TMTD cure system was best for 2nd suppliers medium nitrile and the MBTS and TMTD cure system for 1st suppliers medium nitrile. This was determined by obtaining equivalent physical properties for both polymers and also equivalent resistance to gas permeation. Plant batches of the proven polymers, making use of the forgoing information were mixed. The protectors molded from the two stocks were rejects due to poor moldability.

Along with the work above, in Test #12 the replacement of Silica with SAF Black was reevaluated. The samples made from these stocks looked good as to resistance to gas permeation and indicated by lower Mooney values that processing would be better.

In Test #12 extra samples of all compounds tested were postcured and run along with the others. The better resistance to gas permeation indicated by the postcuring was again indicative that

a tight cure is imperative for low gas permeation.

The next step was taken with the thought in mind to improve processing of the stock. To this point there had not been included a retarder in the compound but in an effort to improve processing by making the scorch time run longer, it was decided to try one. At the same time, stearic acid was included to add a small amount of peptizing and facilitate incorporation of the dry fillers. Both steps were covered in Test #13. Neither showed deleterious effects on resistance to gas permeation, and both indicated some advantage in processing. It was decided to include both chemicals in future work.

The next step (Test #14) was made to incorporate all the points learned from the previous work into a factory mixed compound and check it vs. the old formulation at various cure times. The longer cure times showed the best resistance to gas permeation, but the new compound swelled and blistered similarly to the older. The temperature of test at this juncture was increased to 220°F.

In Test #15 Zeolex 20 was evaluated as a replacement for the Silica in an attempt to improve the processing as well as resistance to permeation. This work indicated the Zeolex 20 to be of no value in a tubing protector compound.

At the same time the Zeolex 20 was checked, further combinations of Silica and SAF Black were evaluated. A 40-part level of Silica and a 35-part level of SAF Black produced a compound with good gas permeation resistance and superior processability to an all Silica loaded stock.

In a further attempt to improve the processing, Test #16 was performed using various levels of FF Black in combination with a low loading of Silica. The higher loading levels of the filler showed the best resistance to the gas, but none of these sample compounds could be considered for use in tubing protectors.

To check out the laboratory results in plant mixed compounds, Test #17 was run. One batch each of two sample formulations were mixed and sample protectors were molded from each. The difference in the two stocks being that the one was all Silica loaded and the other was part Silica, part SAF Black (samples were cut from plant molded protectors). The test pressure here was maintained at 4000 psi at a temperature of 350°F. Both compounds came through this test with flying colors, but it was felt that the high temperature post-cured the samples before the gas had a chance to cause damage. These results warranted a recheck at a lower temperature.

The recheck was made in Test #18. Pieces were cut from both formulas and an old formulation protector and inserted in the gas bomb. This time the temperature was held at 220°F. and the pressure at 3000 psi, The old compound showed the least amount of swell with the mixture of fillers compound next and the all Silica loaded following in that order. This was contrary to previous results and began an investigation into changes made.

At this point, receipt began of a new medium acrylo-nitrile in a Mooney range of 70-80 rather than the previous 80-90. The processing of the lower Mooney polymer was excellent, but the resistance to gas permeation was questionable.

Test #20 through #24 were performed to check out the difference in polymer with the change in Mooney and, if true, to see if a stepped-up cure or post-cure arrangement would not help matters. (With test #20, test sleeves were used as the immersion samples installed on a piece of tubing, giving the same elongation as that of an actual tubing protector.)

These tests pointed out that there definitely was more swell or gas entrapment present when using the low Mooney polymer in the present formulas. It was also found that a cure system of sulfur and Monex was beneficial and that an added post-cure at 350°F also showed improvement.

The low Mooney polymer was so much better in processing that it was felt it was necessary to use it and make it resistant to gas permeation by proper compounding.

Test #25 through #31 were performed with this in mind. All the previous tests were studied thoroughly to pick out the best plasticizers, the best fillers, and the best cure systems, and the optimum levels for each. Such things as magnesium carbonate and Pyrax Wa were tested as a possible means of wicking the gas from the rubber part, but to no avail.

The best system found was to use a combination of Silica and SAF and Thermal blacks with a sulfur-Monex cure and a combination of Dioctyl-Phthalate and Dibutyl-Phthalate as plasticizers. By trying various combinations it was found that high loadings of fillers and plasticizers, which in turn reduced the volume percent elastomer, gave the desired results. As stated previously, the 75 part filler loading was the datum plane and must be maintained above this figure to get good resistance to gas permeation.

This work led to the development of the two new formulations. These formulations were tested in lab mixed and factory mixed samples at a temperature of 220°F. and a gas pressure of 5000 psi. Both came through the tests with an excellent resistance to gas permeation.

The processing of both formulations proved to be excellent. The compound was mixed, all except the cure, in an internal mixer and the cure was added on a 60 in. open mill. The stock subsequently went through the extruding operation in perfect condition and molded with a very small amount of rejects.

Tubing protectors made from plant mixed stocks and extruded loads were tested in 200°F. ASTM #3 oil for a period of 72 hours. They passed this test also.

When a piece from a competitive protector was run along with these formulations in the gas chamber, it increased to five times its normal size due to gas entrapment.

All of the test procedures and design work have proven to give the desired results. The production of a useful product resistant to gas permeation.

It is also a very important fact that this work has been very significant to enable this formulation to be used in many other applications where gases of all types (CO<sub>2</sub>, H<sub>2</sub>S and other hostile gases).

*To err is human,  
but to really  
foul things up  
requires a  
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