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Viton's Impact on NASA Standard Initiator Propellant Properties

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October 2000

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Contents

Acronyms

AMW	average molecular weight
GPC	gel permeation chromatography
JSC	Lyndon B. Johnson Space Center
NSI	NASA standard initiator
Pd	molecular weight distribution
Tg	glass transition temperature
TTA	Thermochemical Test Area
ZPP	zirconium/potassium perchlorate

Abstract

This paper discusses some of the properties of Viton that are relevant to its use as a pyrotechnic binder in a NASA standard initiator (NSI) propellant. Nearly every aspect of NSI propellant manufacture and use is impacted by the binder system. The effect of Viton's molecular weight on solubility, solution viscosity, glass transition temperature, and strength characteristics as applied to NSI production and performance are reviewed. Emphasis is placed on the Viton fractionation that occurs during the precipitation cycle and its impact on bridgewire functions. Special consideration is given to the production of bridgewire slurry mixtures.

Overview

NSI is a widely used pyrotechnic device that has been around for over 30 years and has been assimilated into many devices and spacecraft. Its function is known in the pyrotechnic world as first fire; this means it translates an electrical stimulus into a pyrotechnic action or train. An NSI primarily produces a flame and hot particles that ignite or initiate other powders; but it can be used for its own pressure impulse if there is sufficient pressure impulse present. The propellant used in the NSI is zirconium. Zirconium is a finely powdered metal fuel that is burned with potassium perchlorate, a finely powdered oxidizer, that is mixed and bound together with a Viton-B rubber binder. Specifics for the composition of the propellant are:

Ingredient	% by weight
Zirconium	52.0
Potassium Perchlorate	42.0
Viton "B"	5.0
Graphite	1.0

Until recently, these ingredients were solely blended by hand. The dry powders were poured into a 45-degree-inclined bowl rotating with a Viton/acetone solution. By using the blender, homogeneity was striven for and the solvent was evaporated down. After this the moist solid was sieved in air by hand through a U.S. Standard screen. This solvent evaporation method has been the only mode of propellant blending for production hardware. While this process produces good propellant, it is labor- and hazard-intensive and it relies on frequent manipulations of the mix to produce a homogeneous Viton binder.

A zirconium/potassium perchlorate (ZPP) mixture can be produced by two basic methods. One allows the blending solvent, which has the rubber in solution, to evaporate from the mix, leaving the rubber behind. This is the evaporation cycle. The other produces a precipitation of rubber particles from the blending solvent onto the active particles and decants liquid from the solid mixture. This is the precipitation cycle.

Precipitation employs two different fluids for blending: a solvent for the rubber (Viton) and a countersolvent fluid that makes the rubber drop from solution. The evaporation cycle uses a single fluid: a solvent for the Viton. The most frequently used solvent for Viton is acetone. Acetone readily dissolves Viton, making a viscous solution to which the active ingredients are added. Once a homogenous mix is attained by mixing, the solvent is allowed to evaporate and coat the particles with a film of Viton. This Viton film, which is the binder for the propellant, can significantly affect the propellant's working response. To get consistent and rapid function times, homogeneity is required throughout the entire blend. To assure homogeneity, the binder must be uniformly distributed throughout the mix. In evaporation blends, where the Viton in solution is wanting to move to an evaporating surface with the solvent, care has to be taken to continuously provide new surfaces while there is solvent left to evaporate. Rubber is deposited at these surfaces when the acetone leaves; and this rubber must be kneaded into the entire blend for uniformity. Since it relies on frequent manual movement of the mix during processing to achieve good blends, the evaporation method requires several hours per blend.

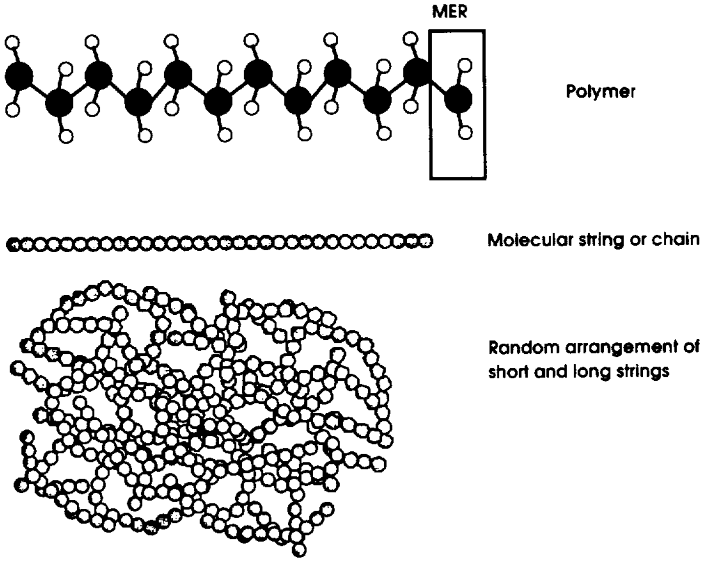
The precipitation blending method relies less on individual blending techniques. The homogeneity of a blend depends more on the mixing apparatus, which can be standardized, and on the standard mixing recipe. The process starts by creating a solution of Viton within acetone, using more solvent than the previous method since evaporation is not a consideration. The solution is placed in a high-speed blender where it is turbulently stirred. While the blender is running, the active ingredients are added and are allowed to mix. When the second fluid or countersolvent is mixed into the spinning mixture, the solution becomes saturated and the Viton begins to precipitate. It comes out of solution using a propellant particle as a nucleus on which to coalesce. The extreme turbulence ensures that all particles are coated with a uniform layer of rubber. Graphite is added into the swirling mass, the countersolvent addition is completed, and the particles are allowed to settle. The clear liquid is decanted off. The wet mix is rinsed with the countersolvent to aid the removal of acetone from the Viton-coated particles and to harden the rubber. The mix is then screened while in a moist or wet state and is separated and dried. Different fluids (including toluene, heptane, hexane, and mixtures thereof) may be used as countersolvents to precipitate Viton from acetone.

Although both blending methods produce excellent propellant, a subtle change in the Viton physics (fractionation) and a seemingly innocuous difference (decanting) between the two methods can significantly affect the firing performance of the propellant, particularly when it is used in a slurry. This difference arises from the Viton binder and its differing properties under various conditions. Because of the pronounced effect of Viton on propellant blending and, particularly, on the slurry process, this investigation was undertaken.

General Description

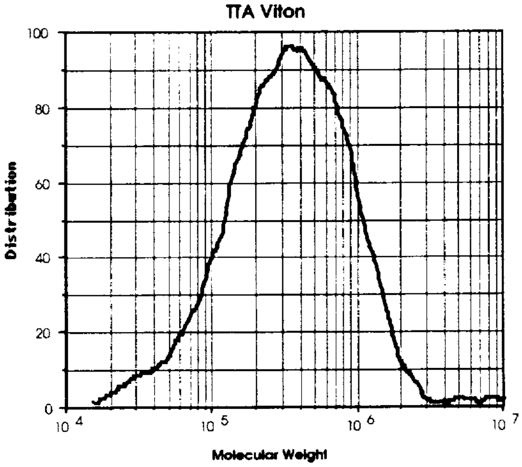
Viton

Viton, a trademark for a series of fluoroelastomers made by DuPont, is available in several formulations (copolymer, terpolymer) and forms (slab, stick, pellet). Like most synthetic polymers, Viton consists of a mixture of high molecular weight, long chain molecules. Not all of these molecules are the same size, however, a condition known in polymers as "polydispersity" (i.e., consisting of many different molecular weights). Polydispersity influences properties important to propellant manufacturing. The building block of Viton consists of repeating subunits called "mers." Mers can be likened to links in a chain. The more links a chain has, the longer the chain is. During the manufacture of polymers, various factors determine the number of links each molecular string will have in its chain. The end result is a mixture of molecules of differing lengths and molecular weights. Often in polymer production, two or more building blocks are used in a reaction. When two monomers are used, the resulting polymer is termed a "copolymer;" and when three monomers are used, the resulting polymer is called a "terpolymer." A mixture of monomers is used to modify the chemical and physical properties of a polymer.



In Viton, monomers contain mostly carbon and fluorine. Elastomeric (rubber-like) materials of this type are called fluoroelastomers. Fluoroplastics and fluoroelastomers are known for their chemical stability. The stability of Viton over time toward oxidizer components of the propellant is paramount. Viton-A is a copolymer and Viton-B is a terpolymer. Viton-B is a rubber polymer built from molecular sections of three separate molecules—i.e., hexafluoropropylene, vinylidene fluoride, and tetrafluoroethylene—that are arranged to achieve molecules of extended length and a broad band of molecular weights. These different constituents have been blended (kneaded) to achieve a uniform set of physical and mechanical properties. Some formulations have fillers and promoters added to modify their properties. One of these fillers, barium sulfate, which is added as a partitioning agent, is undesirable in NSI blends. Owing to the difficulty of separating barium sulfate from the polymer, Viton should be purchased barium sulfate-free.

The Pyrotechnics Group at Johnson Space Center (JSC) has recently performed analyses on several Viton formulations used to manufacture initiators. One of these, TTA Viton, was bought by JSC for propellant blending work and is currently being used in manufacture. The following curve for TTA Viton clearly shows a Gaussian distribution of molecular weights, ranging from approximately 3,000,000 to 15,000 molecular units.



Molecular weight of polymers

Since molecular weight and chain length significantly affect the solubility, solution viscosity, glass transition temperature, and strength characteristics of polymers, they should be carefully controlled. The polymerization process results in varying molecular weights. Differing weights behave differently. Short chains (molecular weight about 10^2) act like a liquid; medium chains (molecular weight about 10^3) yield greases or waxy solids, and long chains (molecular weight about 10^5) produce solids with varying degrees of flexibility. Solids with weights above 10^5 vary in tackiness and stiffness. The lighter ones are more tacky and more flexible.

Using Viton as a binder in NSI propellant formulations requires controls that go beyond a simple specification of Viton-B. Inattention to binder composition and changes that can be made during propellant manufacture can severely impact the quality of the finished product. Owing to the NSI's long history and the fact that several sources are allowed to manufacture it, Viton from different manufacturing lots has been use in production. An analysis of the various lots of Viton was undertaken to confirm that all users were working with the same basic ingredient. Several laboratory tests and gel permeation chromatography (GPC) were used to characterize the Viton constituents. The average molecular weight (AMW), molecular weight distribution (Pd), approximate manufacturing date, and barium analysis for all Viton-B currently used follows.

Sample	AMW	Pd	Date
Hishear Base Viton	501200	1.63	1965
Pacific Sci Base Viton*	440500	2.70	1992
TTA Base Viton	479000	2.45	1988

*Barium sulfate detected by X-ray fluorescence.

Glass transition temperature of polymers

The glass transition temperature (Tg) is the temperature below which a polymer exhibits properties associated with a glass (brittleness). The glass transition temperature is strongly influenced by molecular weight and the degree of crystallinity of the polymer. In general, as molecular weight increases, glass transition temperature increases. Below the glass transition temperature, the coefficient of volume expansion lessens. Shrinkage and expansion are, thus, lower for a given temperature change. This means that less stress is induced from a given temperature change. It also means that the material is also less resilient to any deformation applied; it is "brittle." Having a high Tg can be used to advantage if flex strength is not as important as thermally induced stress. If flexibility at cold temperatures is required, lower molecular weights are wanted. These effects, which may be vital to the functioning of a bridgewire unit, will be discussed later.

Solubility of Viton

Viton is soluble in low molecular weight ketones and esters. The two most widely used solvents for Viton in NSI manufacture have been acetone and n-butyl acetate. In the blending process, acetone is exclusively used as the solvent; and in the slurry process, n-butyl acetate is used predominantly. Viton shows very low solubility in hexane. Solution of Viton in a solvent is accomplished in two steps. In the first, solvent molecules enter the outermost layers and begin to break the polymer-to-polymer attractions. This produces tremendous swelling of the material as the solvent works its way into the matrix with the formation of a gel layer. These gel layers are often difficult to see under poor lighting conditions. In the second, the gel layer slowly diffuses to form a "true" solution. Agitation of the mixture is useful only in speeding up this second step. Since placing a polymer into solution can take a long time, adequate time should be provided for this to occur. The solution process can be quite slow (days) for materials of very high molecular weight. In general, the higher the molecular weight of the polymer, the longer it will take to dissolve in a given solvent (if it dissolves at all).

In solution, a polymer molecule is a randomly coiling mass, most of whose conformations occupy many times the volume of its segments. The size of a molecular coil is influenced by polymer-solvent interaction forces. In a "good" solvent, where polymer-solvent contacts are highly favored, the coils are relatively extended and strung out. In a "poor" solvent, they are contracted in a tight coil. These conformations influence the solution viscosities that polymers show in different solvents. The speed of solution in a given solvent is influenced by how well the solvent can "stabilize" the charges on the molecule. Solubility is influenced by the polarity of both the solvent and the polymer. It should be stressed that acetone will dissolve Viton faster than n-butyl acetate will, but other factors must be considered in the proper choice of solvent.

Solubility in polymer systems is much more complex than in simpler compounds because of size differences between polymer and solvent molecules, system viscosity, and the effects of the texture and molecular weight of the polymer. It is known, for instance, that the topography of a polymer is critical in determining its solubility. Crosslinked polymers do not dissolve; they swell. Lightly crosslinked rubbers swell extensively in solvents in which unvulcanized material could dissolve; but hard rubbers, such as many thermosetting resins, may not swell appreciably in contact with any solvent. This absence of solubility does not imply crosslinking, however. Other features may give rise to sufficiently high intermolecular forces to prevent solubility.

The presence of crystallinity is a common example. The solubility of a single polymer can radically differ, depending on many different variables, some of which are normally considered as negligible or are overlooked.

Fractionation

Precipitation of Viton from a solvent (acetone) by a non-solvent (hexane) results in what is known as "fractionation" or molecular weight separation. As mentioned before, Viton is a mixture of high molecular weight, long chain molecules. When hexane is added, the fraction which precipitates first is the least soluble; i.e., the heaviest molecular weights present in the Viton. Adding more hexane results in precipitation of successively more soluble constituents: the smaller, lighter molecules. At some critical ratio of hexane-to-acetone, the molecular weight distribution of precipitated Viton closely approximates the molecular weight distribution of the Viton originally placed in the solution. At this ratio, the Viton left in the solution is negligible. Although the precipitated rubber will be reconstituted and have the same molecular species, it will not be well mixed. The original Viton was uniformly homogenous. After precipitation, the Viton has been layered into its different molecular weight components. This subtle difference can cause precipitated propellants to behave differently than those that are prepared by the evaporative method.

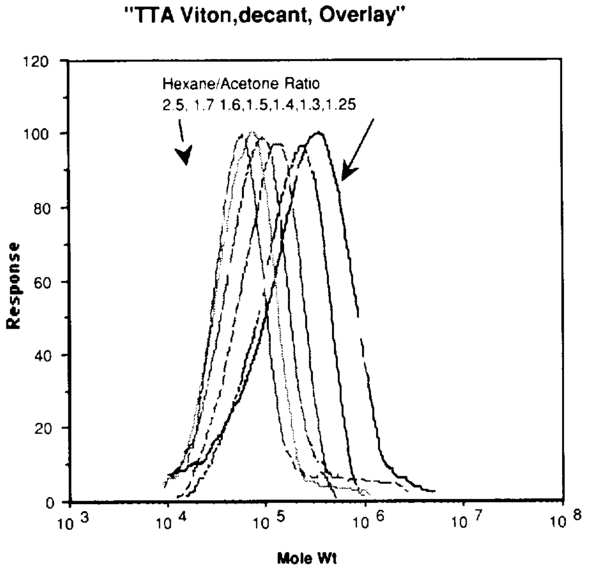
The "critical ratio" mentioned above depends on the molecular weight distribution of the Viton used and, to a small extent, on the dilution of Viton in acetone. The use of lower hexane-to-acetone ratios will result in loss of lower molecular weight species to the decant. The loss of these lower molecular weight species effectively increases the average molecular weight of the polymer. This change will affect the properties of the binder in bridgewire slurry operations. For this reason, each manufacturer should determine the "critical ratio" required for their particular Viton lot and solvent system.

The fractionation effect is well documented in polymer literature. Again, since the solution and the precipitation characteristics of polymers depend upon their molecular weight distribution, the molecular weight distribution should be monitored. Tests performed in the Thermochemical Test Area (TTA) validated that fractionation occurs in the precipitation blending process. The following table shows the AMW and Pd of the polymer lost to the decant at various hexane-to-acetone ratios for the precipitation blending process. This rubber represents a fraction that is no longer available to the propellant.

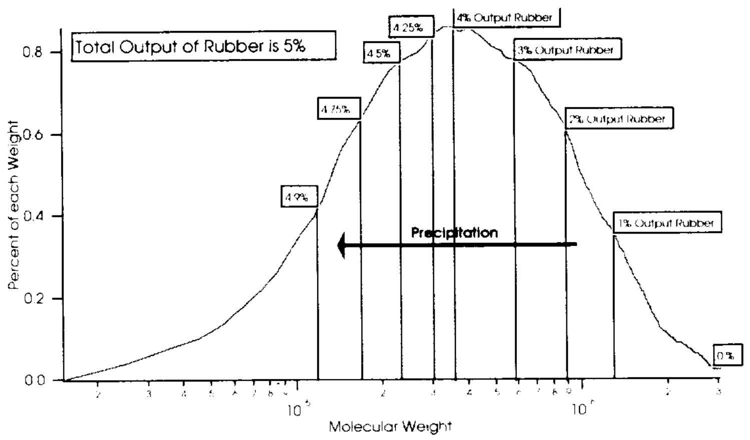
Sample	AMW	Pd
1.25 ratio	394900	2.37
1.30 ratio	245700	1.46
1.40 ratio	162000	1.30
1.50 ratio	145100	1.10
1.60 ratio	123200	1.08
1.70 ratio – limited sample	89200	1.13

It should be noted that each sample vial contained an equal volume of solution. With increasing ratios, more rubber is precipitated and less rubber is present in the decant. At ratios higher than 1.70, the amount of material left in the decant is so small as to complicate the determination of AMW. These values will vary with the AMW distribution of the starting Viton. An overlay of molecular weight curves for each sample is instructive.

The peaks are moving toward the lighter weights and the bands are narrowing. The 2.5 curve ratio (not listed in the table above) is suspected of being contaminated with the precipitate.



The portion of these samples which had precipitated had molecular weights that decreased with an increasing hexane-to-acetone ratio, since a lighter weight fraction of rubber was being added to that already precipitated. Precipitation begins with the heavy weights and proceeds toward the light weights.



The above curve gives the percentage of each molecular weight within the Viton analyzed. The cumulative percentage of all species represented by the area under the curve is equal to 100%. If this area also represents the total amount of rubber (5%) found in the propellant blend, the curve can be used to predict the percentage of Viton (boxes) found in the output and in its molecular constituents. Starting from the right of the graph, the percent of Viton precipitated and the molecular weight composing that percent are shown.

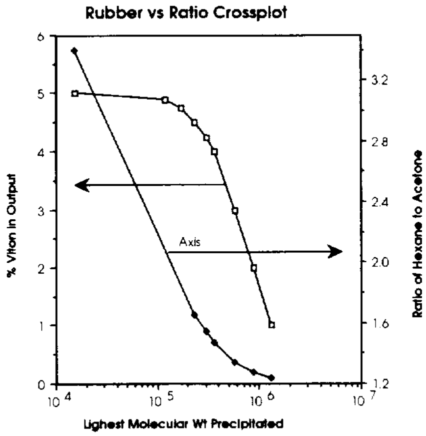
Propellant blending

Under the current manufacturing method, finely divided zirconium and potassium perchlorate are added to a solution of Viton in acetone. During mixing, the particles entrapped in Viton are laid down by evaporation or are precipitated by the addition of a countersolvent such as hexane.

If the process used is evaporation, the Viton is liberated at the evaporating surface in much the same molecular weight distribution as the original rubber. The churning and kneading that takes place in mixing guarantees the various molecular weights are homogeneously dispersed. Once the process is complete, the Viton molecular weights are evenly interspersed with each other (just as they started). Dissolution for the slurry afterwards is no different than that which was used to blend the mix. But if a precipitation method by countersolvent is used, the outcome for the slurry dissolution can differ significantly. By the fractionation process, the highest molecular weight components of Viton in the solvent mixture are precipitated first as a co-solvent (hexane) is added. As hexane addition proceeds, progressively smaller molecules are displaced from solution.

If insufficient hexane is added, the original rubber is never recovered from the decant. This causes changes in the way the rubber will respond to the environment. If the amount of hexane added exceeds a certain hexane-to-acetone ratio (determined by the starting polymer's molecular weight), the precipitated Viton will have the same molecular weight distribution as the starting material but will not necessarily have the same starting arrangement. Since each molecular weight precipitates according to solubility when that species became saturated, the different molecular weights are brought down in layers according to their lack of solubility. This is the "M&M effect."

The "M&M effect" occurs when the least rubber soluble surrounds the active particles. The less soluble fraction precipitates first, but it is the last to dissolve if rubber is placed back into a solvent. Fractionation of the constituents and the loss of low molecular weight species to the decant by low hexane-to-acetone ratios compounds this effect. Fractionation, differing molecular species and subsequent rearrangement during precipitation, can affect polymer properties. This fact must be considered when working with polymer solutions. The following curve shows the interrelationship of the molecular weight, the hexane-to-acetone ratio, and the total rubber in an output blend. It also defines the critical ratio needed for total molecular weight recovery.



Slurry process

The propellant slurrying process used on NSI is much like painting. Paint is a mixture of a solvent, the liquid base for the paint; a solute, the material that, when the solvent has evaporated, acts to hold the pigments onto the part; and suspended particles, the pigments that are carried and fixed by the solute. A simple oil-based paint uses a petroleum solvent with a lacquer solute and colored particles for pigment. Other additives are sometimes added to enhance wetting and flow characteristics. The act of painting applies the liquid matrix to the surface of the part. From that time on, Mother Nature does the rest. If a drop is observed, the following occurs.

The drop has a solvent with a solute material evenly dispersed in solution and a suspension of particles more or less evenly dispersed throughout the liquid. Once the drop strikes a surface, several actions begin. The heavier suspended particles begin to settle against the surface while heating from the part raises the vapor pressure of the solvent. Flow currents are set up to allow higher energy molecules to escape (evaporate) from the available free surface. As the solvent molecules leave, the drop surface becomes richer in solute molecules, driving it to saturation and producing precipitation. The drop surface recedes as the quantity of solvent lessens; and, consequently, a thickening of the suspended particles is left behind in the liquid. The solvent molecules continue to move to the surface, which is evaporating; and since the solute is in the solution, it follows the solvent flow to the surface. At the point below the surface where saturation is achieved, the solute begins to precipitate.

Precipitation occurs over a range of depths, depending on saturation conditions and flow forces. The band of solute particles increases in depth and surface layer until they form a film over the entire surface. Evaporation slows owing to diffusion through this film. The film recedes and contracts with the evaporating surface, laying itself in and over all surface irregularities and anchoring itself to the surface of the part when final drying is achieved. This film covers the once suspended particles, which are left behind, holding them to the surface of the part.

The slurry process is identical to painting. A small quantity of propellant blend, ZPP, is mixed with acetone or n-butyl acetate. The quantity of solid material to liquid is important in order to keep the solution unsaturated in solute. The solute for the slurry is Viton-B. When the solution is unsaturated, all of the solute should eventually be taken into solution. This is important in the evaporation cycle, where it is necessary to achieve a rich (Viton-depleted) zone of ZPP next to the wire. If the ZPP zone next to the wire is not depleted of Viton, energy is used burning rubber off the propellant grains. This causes lengthening of the function time. If insufficient rubber has been removed from the ZPP, the unit may fail to fire.

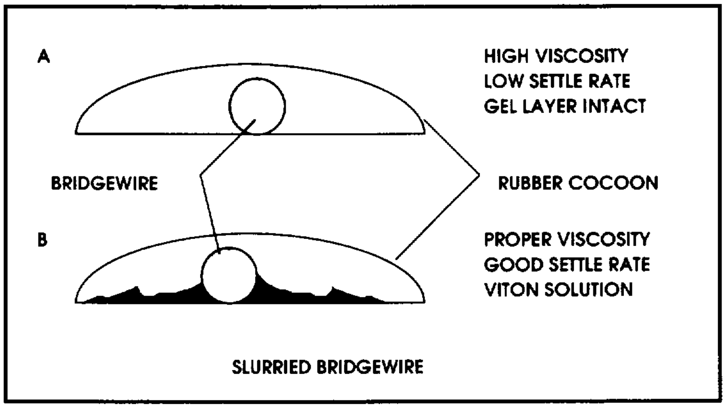
In the bridgewire slurry operation, the propellant that was previously prepared is re-dissolved in a solvent and is applied to the bridgewire. Some manufacturers dissolve the propellant in acetone and others in n-butyl acetate. Either acetone or n-butyl acetate can be used for slurrying. The vapor pressure (evaporation rate) and solubility rate for each solvent differs. JSC testing has shown that acetone will dissolve Viton considerably faster than will n-butyl acetate. Acetone has a higher vapor pressure, evaporates readily, and is faster to swell and dissolve the Viton. N-butyl acetate has a lower vapor pressure and, as a consequence, evaporates slower. It also dissolves the Viton slower. A slurry process must take these properties into account.

If only acetate is used, the propellant must be exposed longer before all of the Viton goes into solution than if acetone is used. Agitation or stirring of the mixture during this solution process is very helpful in speeding break up of the gel layers. A slower evaporation rates requires less makeup solvent during slurry use to keep the solution unsaturated; a longer working time or pot life is thus achieved. Acetone slurry, by contrast, evaporates readily, requires more makeup, and produces a shorter working time for a drop being placed on the wire. Acetone slurry makeup is, therefore, usually done with acetate; i.e., by mixing both solvents to achieve greater pot life and slower drying time for the drop on the wire. It should be noted that n-butyl acetate is considered a nonionic surfactant that assists in separating suspended particles, keeping them from clumping. As a consequence, when the ratio of acetate-to-acetone exceeds 1.0, the slurry achieves a "silky smooth" texture. Once a drop is placed on the wire, it is important to let it evaporate slowly to achieve good separation of the rubber from the active particles. An air-dry is recommended before the units are heated.

Testing has shown that a binder-free propellant is very active and fast. When the wire is activated, the propellant particles are in intimate contact with the heat source. This permits good thermal contact and a fast progression of ignition of the slurry mix and, then, the main propellant slug. If a binder is used, separation of the propellant particles can occur; therefore, energy transfer during ignition between wire and particles can occur, and slurry to main slug can be delayed due to binder thermal separation.

Slurry experimentation has repeatedly indicated the importance of having active particles settle next to each other around the bridgewire to produce a fast unit. Following is an illustration of the effects that the viscosity of the bridgewire slurry mix can have on the "morphology" of the finished unit. It is believed that drawing "B" depicts the more sensitive unit (all other factors being equal).

In principal, this allows for energy transfer to the active particles by direct wire contact or conduction. This is of particular importance during cryogenic (–420°F firings) operations when alternate heat transfer modes, convection, or radiation have minimal effects. Heat is not wasted in raising the temperature of Viton, but it does go to warm the zirconium and to decompose the perchlorate. The slurry works because the Viton is taken into solution in the solvent and, in the act of drying, the rubber is deposited at the evaporating surface. As the rubber moves away



from the active components, it is establishing a binder-free sediment next to the wire. The absence of Viton between the particles next to the bridgewire favors rapid heat transfer and flame propagation. For this situation to occur, the following conditions are required:

1. ***The molecular makeup of the Viton in the propellant blend*** should be a close match to the original Viton in order to maintain the structural and adhesive properties of the binder. The absence of constituents from the binder changes the published and expected properties of the binder. As stated, low molecular weights influence the flexibility (review glass transition) and adhesion of a binder, and heavy weighs influence structure and viscosity. At no time should solvent be removed from the blending or slurry process when rubber is in solution; this results in a loss of molecular species. Evaporation of solvent is the best way to prevent this. If precipitation blending is used, the critical hexane-to-acetone ratio is important. When thermal cycles and cold temperature vibration are performed, loss of low molecular species has shown itself to be deleterious to the slurry on the bridgewire. Reinforcing the missing Viton with an "add-back" system that uses a fractionated Viton/acetone solution for the slurry bowl has proven remedial.

2. ***The solvent used to make the slurry*** must be able to completely dissolve the Viton from the active particles. Taking the Viton to the gel state is not sufficient, since the surrounding gel layer prevents the close approach of particles to one another. Sufficient time and agitation should be used to promote breakdown of the gel layers. Long soaks (from 2 to 3 days) prior to use will assure that the heaviest molecular weights are in solution. While soaking, moving the particles across each other provides an abrading action that helps to disintegrate the gel layers.

3. ***Slurry mixture viscosity as well as the method and speed of application*** play a crucial role in how the slurry reacts. Viscosity affects not only the separation of a binder from the active particles in the evaporation cycle; it also affects the suspension of active particles in the mix itself. The viscosity of slurry is critical. The less viscous the mix, the faster the suspended particles will settle for a given particle size. The larger the particle, the quicker the particle will settle to the bottom. To trap a good distribution of particles in a slurry drop, either the viscosity must be thick enough or a method of constant mixing and rapid application must

be sought to ensure the particles stay suspended in the liquid for pickup by the slurrying drop. If the slurry mix is not viscous enough, the heavier active particles will not stay in suspension longer and will settle to the bottom, it is unlikely they will be picked up. A thin viscosity mix will usually only carry lighter particles forward. Unless sufficient active particles (i.e., zirconium and perchlorate) are present in the mix, sufficient heat may not be released in the slurry to accelerate the flame into the main mix during testing.

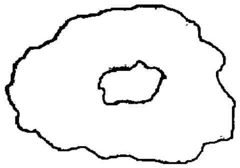
The slurry must be viscous enough to have suspending power to hold the zirconium particles within the liquid while the liquid is being removed and transferred to the bridgewire. However, an overly viscous slurry will impede good rubber migration away from the active components in the drying cycle. If the slurry is too viscous, particles will not settle before the solvent has evaporated and the rubber has hardened; hence, a rubber barrier and slower ignition times will be produced. Here the term "pot life" takes on new meaning.

Pot life provides the time required for suspended particles to settle and for Viton to be carried up and away from the active particles. This provides an insulating cocoon over the bridgewire. Sedimentation of particles in the slurry mixture can be described by Stoke's law. Separation of the zirconium and perchlorate particles during sedimentation may occur under certain circumstances (particle density and size are factors). As the solvent evaporates, the viscosity of the slurry increases as does the time required for the particles to settle.

Slurry mixes with the viscosity of Hershey's chocolate syrup (silky in appearance) or an approximate mix of 2.5 to 3.0 g of ZPP to 1.0cc of solvent when fully in solution. A slurry mass of 2 to 3 mg on the wire gives excellent results. Once applied, this slurry should be left to air-dry undisturbed for 2 hours in order to allow proper separation of the rubber from the active particles. Immediate placement of bridgewire units into an oven to speed the drying process will inhibit the settling of active particles. (Haste makes waste!) Time must be set aside for the particles to settle. The units can be heated for final drying after this.

It is also important to pay attention to the drying process itself. A thin film dries from the outside to the center, with little or no flow in the vertical direction. When the center is drying, the particles are being moved away from each other toward the edge by surface tension; this causes a volume change in the rubber and a bare spot to form in the geometric center. A thick film dries from the edge to the center, but it also dries from top to bottom as well. The flow and surface tension forces carry the smallest, easiest to ignite particles with it. Differing properties mean the heaviest weights will have a strong tendency to solidify first and form a structural tent over the drop. The light weights—owing to their light weights, solubility, adhesion characteristics, and surface tension—will solidify later but will maintain a hold on the active particles the longest and will attach themselves and the particles to the underside of the tent. This process removes particles from the bottom and center, leaving a tunnel or gap in the slurry cocoon.

In-house testing has shown that fractionating the rubber toward lighter molecular weights improves the slurry drying process. Lighter weight species need less solvent to reach the chocolate syrup viscosity range and are more tacky and pliable when solidified. The heavier weights need more solvent because they are bulkier and appear to be more viscous, are harder to maintain in solution, and are more rigid when dried. Because of these differences, there is more volume contraction on drying with the heavy molecular weight slurry than with a slurry of light weights and significantly more cracking.



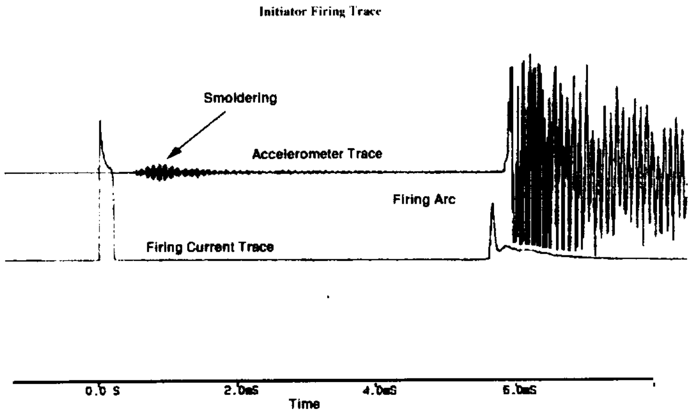
Drop

Cocoon

Since the electrical center of bridgewire, which is identical to its geometric center, is the hottest spot and the start of initiation, intimate contact with the smallest particles is desired. But if a gap or a tunnel is present, initiation is stopped or delayed until the larger particles are brought up to temperature. To preclude this, multiple thin layers should be applied. The first drop with a light viscosity needs to flow easily and to wet the entire wire before it is allowed to dry. Drying should occur from the outside to the center, with no separation around the wire. Subsequent drops should have higher viscosity and should be applied over the first wire to add mass and thermal isolation.

4. ***A sufficient load of active particles in the slurry*** must be delivered to the bridgewire. Heavy active particles will settle in the slurry container or dish. Be sure to stir the slurry supply regularly. The dish should be shallow (0.5-inch deep) to allow proper agitation to re-suspend the particles. The slurry drop should be "flowed" or applied onto the bridgewire by means of a toothpick or a small brush. The brush is not recommended since residues from one drop to the next can cause erratic results. A toothpick that can be wiped clean from one unit to the next gives the most consistent results. Remember that viscosity changes due to solvent loss or temperature changes can affect particle uptake.

It is important to note, when testing an initiator, whether the firing current trace shows a low-level reaction (smoldering) occurring prior to ignition of the explosive main mix. If it does, this indicates a slurry problem. Either the zirconium particles have settled in the slurry bowl and are not carried forward to the slurry drop, or insufficient mass has been applied (thin slurry), or the rubber has not been totally removed from the active particles (thick slurry or Viton not in solution). All of this is easy to say but difficult in practice. The production of a fast bridgewire is an art that needs constant attention and practice.



Bridgewire Slurry Addendum

Bridgewire slurry operations are key to the production of NSI hardware. During this operation, a mass of propellant is placed in a solvent to dissolve the binder. The resulting paint-like mixture is used to coat the bridgewire filament. A laboratory study was performed to better understand this process.

Due to the small size of the bridgewire unit and lack of access within the charge cup, a mockup using glass slides on a special microscope stage was used in the laboratory study. Microscope observations revealed crevices and pockets forming next to bridgewire on drying; in some cases, these were large enough to cover the entire bridgewire filament. Several crevices severely reduced heat transfer from the filament to the slurry mass. These defects can be responsible for many "long to fire" or "fail to fire" conditions. The participation of one manufacturer in this study verified that live blends used for slurry operations produce these same type of voids.

Voids are caused by stresses developed in the coating as it dries. After the slurry mixture is applied to the bridgewire, the slurry forms an outer skin which gradually thickens. This outer shell must collapse upon the shrinking drop as solvent leaves the slurry droplet. Under certain conditions, this upper shell may become so rigid that it cannot collapse owing to its increasing viscosity and solids loading. This inability to collapse when the droplets are shrinking places the underlying structure in tension. The amount of stress developed is a function of the solvent volume that is left in the droplet when the upper shell becomes rigid. Depending on the drop's geometry (thickness), sufficient force may develop to lift the "floor" of the drop towards the upper shell, thereby causing voids to occur around the bridgewire. Since this situation cannot be observed from the top of the slurry droplet, it may go unnoticed.

Currently, it is known that the molecular weight of the Viton in a propellant can influence this behavior and that certain measures can be taken to prevent void formation. One such measure is to make the bridgewire slurry less viscous by adding extra solvent to it. When such a slurry is added to the bridgewire, it tends to spread out more and to reduce the thickness of the droplet. The first application must not attempt to provide the necessary slurry mass and should be viewed as a primer. This method works because it reduces the thickness of the droplet and, thus, reduces the stress (top to bottom) produced in the drying film. Another way of viewing this fix is that insufficient thickness needs to exist in order to form a rigid outer shell. Using this fix requires that subsequent applications be applied atop the first to achieve sufficient slurry mass. Subsequent drops need to be more viscous for mass loading and to prevent resolutionizing the first application.

A second method of reducing voids relies on subtle effects caused by the molecular weight of a binder. In preliminary testing, this method has produced the most void-free slurry droplets observed. It calls for a slight reduction in the molecular weight of the binder used in a slurry. This is achieved by a mini-blend for the slurry of the same ingredients as the main blend with fractionated Viton. Eventually, the blend may include the entire propellant. While this method changes the molecular weight of the binder, it does not change the percentage of binder in the propellant. An explanation of why it works follows.

The viscosity of polymer solvent solutions is strongly influenced by the molecular weight of a polymer in solution, not just its concentration. In general, the higher the molecular weight of a polymer, the more viscous the solution will be. So, if 10 g of heavy molecular weight Viton are added to 200 ml of acetone and 10 g of low molecular weight Viton are added to 200 ml of acetone, the solution made with the high molecular weight Viton will have a higher viscosity.

Viscosity is critical in the bridgewire slurry operation. A slurry that is too thick does not leave the applicator, and a slurry that is too thin drips from the applicator before it can be positioned. As a consequence, most of the manufacturers are working within a viscosity "corridor." The ideal viscosity is achieved by experience. If a mixture is thick, a little more solvent is added. If a mixture is too thin, some of it is allowed to evaporate. What determines how much solvent a slurry must contain is the molecular weight of the Viton in the propellant. If a high molecular weight Viton is used, more solvent is added since solutions made with high molecular weight polymers have an effectively higher viscosity. If a low molecular weight Viton is used, less solvent is added because solutions made with low molecular weight polymers have an effectively lower viscosity.

The impact of these statements becomes apparent when we realize that the stresses developed during slurry droplet drying arise from solvent loss. Slurries made from low molecular weight Viton have less solvent in them (to achieve the right viscosity); i.e., approximately half of that for the heavier molecular weights. They, therefore, have less solvent to lose. Less solvent to lose means lower stresses and fewer dimensional changes during drying. Since lower molecular weight Viton is less likely to form a hard shell incapable of movement during the drying process, it should retain more of its flexibility at low temperatures. By lowering the molecular weight of Viton, it becomes easier (wider corridor) to apply an application of slurry to the bridgewire without cracking.

By applying the methods described here, NSI units have been prepared that function at less than 400 μs with little deviation. Further testing must be conducted to determine what effect a lowering of the overall molecular weight of Viton will have on the propellant as a whole.

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13. ABSTRACT *(Maximum 200 words)*

This paper discusses some of the properties of Viton that are relevant to its use as a pyrotechnic binder in a NASA standard initiator (NSI) propellant. Nearly every aspect of NSI propellant manufacture and use is impacted by the binder system. The effect of Viton's molecular weight on solubility, solution viscosity, glass transition temperature, and strength characteristics as applied to NSI production and performance are reviewed. Emphasis is placed on the Viton fractionation that occurs during the precipitation cycle and its impact on bridgewire functions. Special consideration is given to the production of bridgewire slurry mixtures.

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