



Cable Rejuvenation Mechanisms: An Update

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SUMMARY

Recent advances in cable life extension technology have demonstrated a greater than three-fold life improvement over earlier generations. This paper provides an update to a 2006 “Cable Rejuvenation Mechanisms” paper providing the most up-to-date fluid formulations and performance data.

The greater than three-fold performance improvement of 732 technologies over the previous generation of rejuvenation approaches does not result solely from the benefits of providing an adequate volume of fluid and adjusting the formulation to the geometry and anticipated cable operating temperature profile discussed in previous papers [1], [5], and [6]. As important as those advances were, this paper demonstrates a theoretical framework and provides data, which gives new insight into the observed three-fold performance improvements. The 732 technology performance advantage is explained by ...

- tailored volume and tailored formulations for each cable geometry and operating temperature, in contrast to the historical method where the amount of fluid supplied is what conveniently fits in the cable, and a one-size-fits-all chemistry is applied to disparate applications;
- superior functionality for micro-void filling and drying;
- completely new functionality for stress grading, voltage stabilization, UV stabilization, anti-oxidation, and PD suppression;
- long-term treatment persistence provided by catalyst-silane systems, which retain the required quantity of dielectric enhancement fluid in the cable at the required concentration for the required time.

The 011 fluid enjoys an incremental medium-term performance gain due to the mechanisms cited above except that the formulation is not tailored to circuit conditions. There is no long term stress grading, voltage stabilization, or anti-oxidation, and there is very limited PD suppression and UV stability functionality. Accordingly, circuit owners should only consider 011 technology for non-demanding applications.

KEYWORDS

Aging Underground Cables, Underground Cable Life Extension, Underground Cable Rejuvenation

1. INTRODUCTION

In [1] Bertini and Vincent demonstrated a significant mismatch between the fluid required to adequately rejuvenate typical URD cables and the fluid supplied by the previous generation of technology. The previous generation of technology described in [2], [3], and [4] was conceived, reduced to practice, and commercialized by Bertini, Vincent and their colleagues and is referred to as ‘841. In [1], Bertini and Vincent introduced a new injection technology, which eliminated the inadequate fluid supply issue and provided data demonstrating short-term performance gains 87 times superior to their previous technology. In a two-part paper, [5] and [6], data and a model were provided, which focused on the long-term performance of earlier technology and the new developments referred to as 732. In experiments with matched protocols, where each identifiable deviation from matching favored the older technology, the new technology provided over three times the post-injection longevity.

The greater than three-times improvement in performance cannot be explained entirely by the undersupply of fluid common with the ‘841 approach. The published performance of the ‘841 technology was for a 20kV, 240 mm² round strand cable. As shown in [1] and [4], 240 mm² round strand cable is the optimum case for the ‘841 approach, and fluid supply was not a factor contributing to its three times shorter life.

This paper provides an update to the theoretical framework and supporting data for the observed three-fold performance difference first published four years earlier in [7].

2. CABLE FAILURE

Figure 1, taken from [7], provides an overview of cable aging and failure mechanisms (square rectangles) and the mechanisms by which cable rejuvenation (rounded rectangles) interfere with aging and failure.

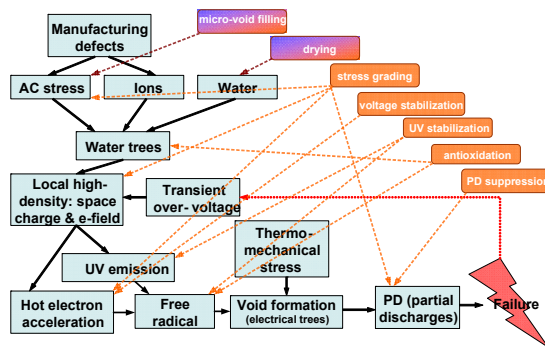


Figure 1. Cable aging, failure and rejuvenation mechanisms.

Ingredient			Comment/Purpose
'841	011	732	
TMMS	2-ethyl-hexanol		short term
PMDMS		TEMDMS	medium term
TIP		DDBSA	condensation catalyst
		CBMDMS	long term; stress grading
		123	HALS UV stabilizer
		1130	UVA stabilizer
		GA	voltage stabilizer
		ferrocene	PD suppression; UVA stabilizer
		KV10	antioxidant

Table 1. Ingredient comparison of '841, 011, and 732 technologies.

3. REJUVENATION DIMENSIONS

To assess the post-injection performance of a rejuvenation technology, it is necessary to consider two dimensions. The first dimension includes the functional mechanisms by which the treatment fluid interferes with the aging and failure processes. The second dimension is the persistence of those functions with time, which will be discussed after the seven mechanisms of the first dimension are described.

Figure 1 shows seven rejuvenation mechanisms (as rounded rectangles) along with arrows, which indicate the step(s) of the aging and failure process mitigated by each rejuvenation mechanism. The next seven sections of this paper will examine each of these mechanisms in some detail.

Three commercially available technologies are compared. The older '841 injection technology provides only the first two mechanisms, namely micro-void filling and drying. An improved version of the older chemistry, coded as 011, includes the same two mechanisms as '841, but has improved persistence and provides modest UV stabilization and slightly improved partial discharge suppression. In contrast, 732 technology derives performance benefits from all seven mitigation mechanisms.

Table 1 provides a summary of the three ingredients utilized by the older '841 approach alongside the analogous and additional ingredients of the 011 and 732 technologies. There are six ingredients in the 732 technology which have no analog in the '841 formulation. In Table 1 and throughout this paper, TMMS is trimethylmethoxysilane, PMDMS is phenylmethyldimethoxysilane, TEMDMS is tolylethylmethyldimethoxysilane, TIP is titanium(IV) isopropoxide, DDBSA is dodecylbenzenesulfonic acid, CBMDMS is cyanobutylmethyldimethoxysilane, 123 is Tinuvin[®] 123, 1130 is Tinuvin[®] 1130, GA is geranylacetone, and KV10 is Irgastab[®] Cable KV10. Tinuvin and Irgastab are registered trademarks of BASF.

4. MICRO-VOID FILLING

Not to be confused with voids, which can be imaged with an optical microscope, micro-voids are on a much smaller scale. These micro-voids are usually chemical imperfections in the polyethylene characterized by the presence of bonded oxygen, often carboxyl-groups, which have a greater affinity for water relative to the hydrophobicity of non-treed PE. The silanes used by the '841, 011 and 732 technologies react with and displace water at oxidized PE sites within the water-trees. The replacement of conducting ionic water with a silicone dielectric increases the dielectric strength of the insulation. This effect is easily demonstrated using standard water-tree staining techniques. Thick samples of treated cable do not easily stain with methylene blue. Only after prolonged boiling is the silicone driven off leaving the methylene blue free to react with the oxidized polyethylene. While the '841, 011, and 732 technologies work similarly, the TEMDMS of 732 was designed to have a higher affinity for polyethylene. In fact, TEMDMS has the same molecular structure and functionality as the PMDMS of the '841 and 011 fluids, except that it contains three more methylene (-CH₂-) units strategically arrayed about the aromatic phenyl group. Since the aliphatic methylene groups are more soluble in aliphatic PE than the aromatic phenyl group – like dissolves like, the affinity of TEMDMS and its aromatic oligomers for polyethylene is increased compared to PMDMS. . For example at 22°C TEMDMS is 12% more soluble in PE than PMDMS.

5. DRYING

There are two drying effects. The first, the chemical reaction of methoxy silanes with water yielding methanol as a by-product, is the most widely reported in past literature but is the least important of the two effects. [6] and [9] demonstrate methoxy water-reactive functionality is very short-lived. Even in the most favorable circumstances, the methoxy functionality is effectively consumed in less than two years for all of the silanes in Table 1. At higher soil or operating temperatures, water reactivity may be depleted in two months.

Much more important than the transient chemical drying is the ability of the treatment to reduce the reentry of water. To this end, materials that have an improved affinity for polyethylene, such as TEMDMS and its oligomers, provide superior water repellent capability. The molecular thermodynamics of this phenomenon are discussed in [6]. If high affinity for PE were all that were required, a chemist would choose an aliphatic organic, however, the second dimension, treatment persistence, discussed later in this paper, trumps the first dimension. The high affinity material must also stay in the cable for the desired post-injection lifetime in sufficient concentration to preclude significant water reentry.

6. STRESS GRADING

The inclusion of high dielectric constant layers to grade the electric field within cables and cable components is widely practiced and well understood. As modeled in Figure 2, cable rejuvenation with

732 allows for the introduction of carefully chosen high dielectric materials, which provide stress grading on a micro-scale where highly divergent electrical fields create strong dielectrophoresis effects. Materials such as water are drawn to such locations because of the great difference between their dielectric constants and that of PE. The Clausius-Clapeyron equation predicts this behavior.

Table 2 provides dielectric constants for selected materials. The difference between the dielectric constants of PMDMS or TEMDMS and their respective oligomers with that of PE is not sufficiently high to provide a significant dielectrophoresis effect or a stress grading effect.

On the other hand, CBMDMS and its oligomers, enjoy a strong dielectrophoresis effect. This effect draws them to precisely the locations where they are needed. Once at the locally high stress region, these high dielectric constant materials smooth the highly divergent electrical fields. Referring to Figure 1, localized stress grading interferes with at least four portions of the failure mechanism.

1. The local AC stress is reduced, and water trees grow more slowly.
2. The high electrical fields around space charges are reduced, which reduces the likelihood of UV photon creation and the inception of free electrons.
3. Any free electrons will not be accelerated to the same energy as they would have been in a greater field.
4. The reduced local field increases both the partial discharge inception and extinction voltages.

Stress grading functionality is entirely absent from the chemistry of '841 and '011 fluids.

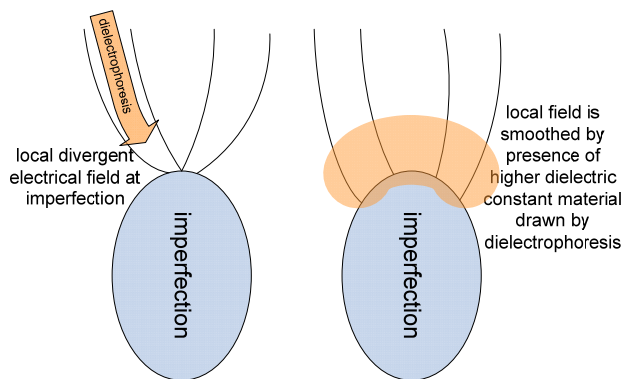


Figure 2. Model imperfection with divergent electrical fields, dielectrophoresis, and the resulting local concentration of high dielectric constant material.

Material	Dielectric Constant
air	1.0
water	78.0
PE	2.3
PMDMS & TEMDMS	3.2
CBMDMS	>20.0
acetophenone	17.3

Table 2. Approximate dielectric constants of selected materials at 60Hz and 25°C. Oligomers of silanes are about the same as the monomers

7. VOLTAGE STABILIZATION

The effects of voltage stabilizers such as ketones are due to keto-enol tautomerism or similar resonant structures which have been described, for example, in U.S. patent 3,445494 and utilized in [10] and [11], for instance. Resonant structures provide a stable receptor for the energy of hot electrons. For example, the more stable keto form of the voltage stabilizer absorbs much of the energy of hot electrons and converts through electron redistribution and proton migration to the higher energy enol form. The enol can then convert back to the keto form with the evolution of heat energy, regenerating the voltage stabilizer. This process prevents hot electrons from causing damage through the production of free radicals.

Because of their greater polarity, ketones also show preferential solubility in water treed portions of the insulation, due the presence of similar carboxyl and hydroxyl functionality associated with water trees, so the ketones tend to concentrate in the areas where they are most needed. The 732 technology includes an unsaturated ketone, geranylacetone, tailored to intercept and thermalize hot electrons.

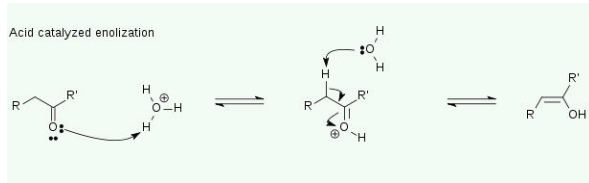


Figure 3. Keto-enol tautomerism and electron thermalization. R and R' represent the balance of the ketone.

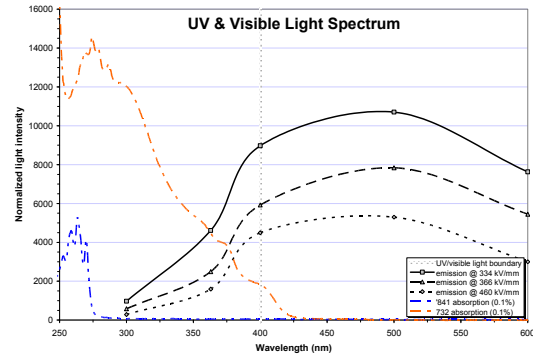


Figure 4. UV and visible light emitted (0=background) from charge recombination in PE defects and absorbed (0=transparent) by treatment fluids at 0.1%_w concentration.

8. UV STABILIZATION

Figure 4 shows the spectra of visible and UV light emitted from charge recombination near defects as reported by [12] at three different local electrical stress levels. A portion of the full UV spectrum (10 to 250 nm) is not displayed in Figure 4. Although the UV spectrum encompasses wavelengths of 10 to 400 nm, there are no significant emissions of UV light at wavelengths shorter than 275 nm [12]. While the phenyl groups of PMDMS and TEMDMS do absorb within the UV range, that absorption occurs below the range of the relevant UV emissions, which range from 275 to 400 nm. The PMDMS component of the '841 and 011 fluids plotted in Figure 4 is essentially transparent to UV in the relevant range. The TMMS component of the '841 material, lacking any conjugated double bonds, is entirely transparent to UV and dilutes the already weak UV absorption of the conjugated PMDMS component.

In contrast, '732 technology includes components, called ultraviolet absorbers or UVA for short, which absorb photons in the 275 to 400 nm range. Specifically, ferrocene and 1130 provide the appropriate absorption. Ferrocene and 1130 are each quite soluble in PE and EPR but diffuse slowly. Their beneficial UVA effects persist for over 4 decades in most applications. Over the range of UV photons emitted by water trees, the '732 technology absorbs from 31 to 181 times more UV than the PMDMS utilized by the '841 and 011 fluids at the same concentration.

In addition to the UVA components in '732, both '732 and 011 fluids include 123, a hindered amine light stabilizer or HALS. HALS are free radical scavengers that trap radicals before subsequent reaction leads to polymer degradation. As demonstrated in [13], HALS are self-regenerative. After quenching a free radical, the HALS regenerate and can then quench another free radical. UVA and HALS enjoy a chemical synergy. Since UVA materials attenuate but don't completely eliminate UV emissions, there will always be some UV photons which damage the polymer. That is where the HALS come to the rescue. By themselves, HALS would be overwhelmed if 100% of the UV photons emitted contacted them, but they can efficiently dispose of the remainder of UV photons not eliminated by the UVA. Together UVA and HALS provide greater UV stability than either one alone. The optimum combination of UVA and HALS is found only in '732 technology.

9. ANTIOXIDATION

Antioxidants are included in virtually all modern cable compound formulations. While originally deployed to prevent oxidation during the extrusion process, it has been shown in [14] that antioxidants also slow the growth of water trees. It has also been demonstrated in [15] that the presence of antioxidants increases the electrical tree inception voltage. KV10, a sulfur containing phenolic antioxidant, has been demonstrated to slow the growth of water trees by a factor of four. The class of sulfur containing phenolic antioxidants has been shown to increase electrical tree initiation voltage by

up to 75% at just 0.2%w. KV10 enjoys a very high solubility in polyethylene and EPR and because of its high molecular weight of 424.7, a very low diffusion rate. The combination of high solubility and low diffusivity yields a very low sweat out or exudation as was shown in [14]. Antioxidants are not present in '841 or 011 fluids. KV10 is present in 732 fluid.

10. PD SUPPRESSION

There are several mechanism involved in the suppression of partial discharges or PDs. First, as described previously, local stress reduction through stress grading increases the partial discharge inception and extinction voltages.

As described in [16], a free electron, often from cosmic rays, is a necessary precursor to the initiation of a PD. Therefore, a second suppression mechanism is provided by the electron affinity of the voltage stabilizer (GA) described in [10] and [11] and the electron accepting ferrocene as shown in [17].

The ferrocene compound included in the 732 technology also provides third and fourth mechanisms. The presence of ferrocene prevents the inception of partial discharges through a partial ionization process outlined in [18]. This renders the walls of large voids partially conductive when voltages exceed a threshold well below typical inception voltages. Once the walls are partially conductive, the e-field all but disappears. In the event that a PD does occur, a small portion of the ferrocene is consumed, simultaneously raising the pressure in the void and releasing an oxygen scavenger, namely atomic iron. These effects act to quickly snuff out incipient partial discharges and mitigate the damage normally incurred when a discharge occurs.

11. TREATMENT PERSISTENCE

None of the seven mechanisms described above have much practical value, unless the effect can be sustained over the desired post-injection lifetime of the cable. The post-treatment persistence is the most challenging requirement of a rejuvenation technology that extends the reliable life of a 25 to 40 year-old cable for another 40 years. The accelerated testing and modeling of rejuvenation technologies was detailed in [5] and [6]. The '841 technology includes two components. The first component is TMMS. TMMS represented about 30%_w [3] of the composition from the introduction of the '841 technology in 1994 until 2005, when the concentration was reduced to between 5%_w and 10%_w according to the current MSDS [19] provided by the supplier. TMMS is a highly soluble and quick to diffuse component, which, at least at the higher historical concentration, provided the short-term (i.e. 3-24 months after injection) performance boost reported in the literature [3]. The higher concentration of the TMMS component also assured adequate symmetric penetration. The optimum concentration of TMMS for '841 is "*greater than 10%_w and preferably about 30%_w*" from [3].

Based upon the data and discussions of [3], the 2005 '841 formulation change will hamper the short-term performance and lead to asymmetric penetration profiles, thereby reducing the treatment efficacy. This formulation change was implemented to reduce the likelihood of corrosion of aluminum strands described by [20] and experienced by the '841 chemistry as discussed in [21] and [22].

The second '841 component, PMDMS represents the bulk (about 70%_w to 95%_w) of the formulation and, for less demanding (i.e. low-load and cool-soil) applications, can potentially provide acceptable medium term (i.e. 1-10 years) performance as demonstrated by [6]. At least for non-demanding applications, the 011 fluid extends the medium-term performance of PMDMS beyond 10 years with previously described, improved injection methods, and with proper catalysis as explained below. The 732 technology adds entire functional elements not found in the '841 and 011 fluids, but the over three-fold increase in longevity requires one more dimension to clarify the profound performance difference.

Alkoxysilanes (i.e. the '841 and 011 silanes and the 732 silanes) undergo two types of chemical reactions, both of which typically are accelerated by catalysis. The first reaction type is hydrolysis. The second reaction type is condensation. The condensation reaction does not occur at an appreciable rate without the presence of catalyst in sufficient concentration. For example, Vincent demonstrated in [2] that, without catalyst, there was no measurable condensation of PMDMS in 2,108 hours in a test tube at 25°C.

In other words, if there is an inadequate quantity of catalyst permeating along with the silanes and siloxanes of a treatment fluid, there will be little or no condensation, and the monomers will exit the cable in months, not years. The fugitive nature of these uncatalyzed monomers means that any performance benefit is short-lived when compared to a desired life extension of 20 to 40 years. This effect was demonstrated in [5] and [6] and is consistent with the data presented by Kleyer and Chatterton in [23]. The data and analysis demonstrate that in excess of 25%_w of the TIP catalyzed PMDMS monomer permeates into the soil without undergoing any condensation.

Diffusion data from [3] and [7] for TMMS, PMDMS, and TIP demonstrate that PMDMS monomer diffuses about 5.8 times faster than the catalyst required for it to condense. At that same temperature, TMMS monomer diffuses about 26 times faster than the TIP and is effectively precluded from any condensation reaction. With the TMMS component, representing between 5 and 30%_w of the formulation (depending upon the vintage of the injection), essentially leaving the cable without condensation occurring and 25% to 39% of the PMDMS monomer doing the same, between one-third and one-half of the '841 treatment fluid has no influence on the medium-term or long-term post-injection performance.

The retention efficiency may be expressed as a percentage of any monomer-catalyst combination as X_o/X_i . X_o is the mass fraction of the monomer that is not lost from the system before condensation, less the non-functional hydrolysis by-products (typically methanol). X_i is the mass fraction of the fully oligomerized monomer less the non-functional hydrolysis by-products. The hydrolysis by-product for pure PMDMS, for example, calculated from stoichiometry is 25.3%_w methanol. Thus a perfectly catalyzed system, which loses no uncondensed monomer, would enjoy 100% retention efficiency.

Retention efficiency can be measured in full-size cables as in [23], but considerable time is required to obtain the data. Miniature or model cables can be utilized to obtain results in a more timely fashion. The model cable is filled with fluid and catalyst combinations in the same proportion as with full-size cable, and the weight of the sealed assembly is monitored with time as fluid exudes from the cable. The model cable is temperature controlled in a water bath to simulate buried cable or in a bed of diatomaceous earth to simulate a dry environment for control purposes only.

Figure 5 presents data collected to measure retention efficiency from a 1/6th scale model of a 15kV cable with 100% insulation and a 53.4 mm² (1/0 AWG) conductor for the PMDMS/TIP system ('841) in historically widespread commercial use. The horizontal line at 74.7%_w shows the best possible retention after accounting for the unavoidable loss of methanol as PMDMS hydrolyzes. The dashed line delineated with diamonds shows how the monomer quickly exudes if there were no water available to allow hydrolysis to occur, since hydrolysis is a necessary precursor to condensation. Finally, the smoothed line with triangles shows the performance when catalyst is added, and the model cable is submerged in 55°C water. The point at which the silane/catalyst system plateaus is 45.6%_w. The retention efficiency for this system is 61%_w (i.e. 45.6/74.7). The retention inefficiency or portion of the treatment fluid that leaves the cable very quickly and does not provide any medium or long-term benefit is 39%.

In contrast to the 61% retention efficiency of the '841 technology, the 732 technology enjoys a 98% retention efficiency. The data is provided in Figure 6 with each line being analogous to the lines described in Figure 5. Note that the MeOH loss line starts with about a 5%_w stoichiometric advantage over PMDMS. The 011 technology uses the same advanced catalyst system as the 732 approach.

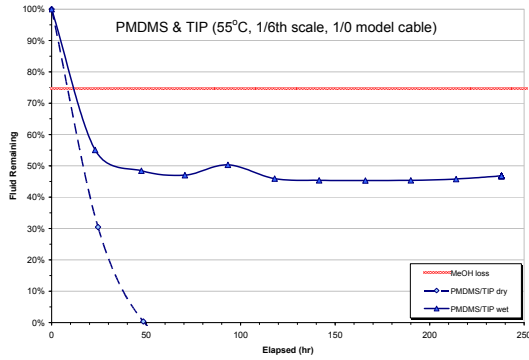


Figure 5. Siloxane retention data for PMDMS & TIP at 55°C. Exudation inefficiency is 39%.

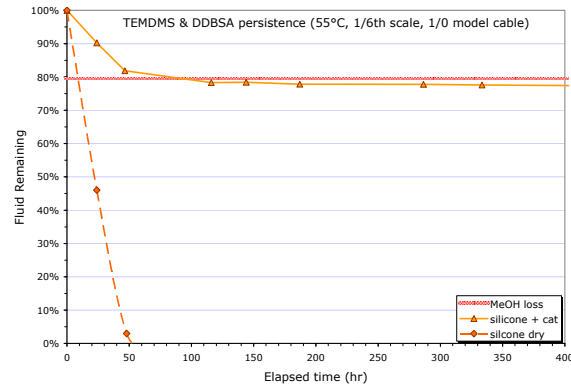


Figure 6. Siloxane retention data for TEMDMS & MSA/DDBASA at 55°C. Exudation inefficiency is 2%.

As described in [1], the ‘841 injection approach undersupplies fluid for URD-sized cables (round conductors less than 125 mm² or 4/0 AWG) and even some larger conductors where the strands are compressed or compacted. For example a 15kV, 19-strand, 53.4 mm² (1/0 AWG) cable suffers from an undersupply of fluid by about a factor of two before dilution of the medium term treatment fluid with the fugitive TMMS. The entire TMMS portion of the ‘841, which is between 5%_w and 30%_w of the formulation, is fugitive and has no impact on medium or long-term performance.

As described in [24], these same cables treated with ‘841 technology lose 5%_w to 15%_w of the supplied fluid to the EPDM components through which the fluid is injected. If there are any splices in the cable, there is an additional loss not reflected in [24]. No such losses occur with 011 and 732 technology, as impermeable injection adaptors are utilized as described in [24].

Because of the 011 and 732 supply flexibility described by [1], precisely the required amount of fluid can be supplied to almost any cable to achieve the desired post-injection performance. For the 53.4 mm² (1/0 AWG) cable provided as an example in Table 3, the total supply differences between 732 or 011 silanes and the ‘841 silanes are about four-fold. For smaller cables, such as those with 7-strand, 33.6 mm² (No.2 AWG) conductors or for cables with compressed or compact conductors, the total supply difference becomes greater. For larger cables the difference diminishes, but the medium term component difference never drops below the difference in retention efficiencies.

The 732 technology also includes several long-term performance ingredients, which have no analog in the ‘841 and 011 approaches. For the PMDMS of ‘841 fluid and 011 fluid, and the TEMDMS component of the 732 formulation, a point in time is reached when the oligomer concentration declines below the threshold performance level described in [5] and [6] of 16 kV/mm (400 v/mil). Performance above this threshold level is sustained by the medium-term component of 732, TEMDMS, for considerably longer than that of ‘841. Ultimately, however, TEMDMS and its oligomers decline in concentration, and if there were no long-term components, the formulation would experience dielectric enhancement efficacy approaching the reliability threshold. It is at this point when the slow to permeate long-term components of 732 (i.e. CBMDMS, GA, 123, 1130, KV10, and ferrocene) begin to engage and sustain reliability above the required threshold. These long-term components are entirely absent from the ‘841 technology and absent or available at lower concentrations in the 011 technology as summarized in Table 1.

12. CONCLUSIONS

Over the last twenty-five years, rejuvenation technology has evolved to extend cable life up to 40 more years, even for cables at the end of their useful life. Advances in process, which deliver the enhancement fluids in more efficacious ways, and advances in chemistry, which address the full spectrum of cable degradation mechanisms were both required. In the final analysis cable life extension is dependent upon the persistence of the treatment fluids in the cable’s dielectric. This last

advancement is perhaps the most important and was realized with the introduction of an entirely new class of catalyst with near perfect catalytic efficiency.

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