

# Rejuvenation Reformulated

Glen J. Bertini and Gary A. Vincent  
Novinium, Inc.

**Abstract:** Over the last two decades the economical phenylmethyl-dimethoxysilane (PMDMS) has been used to extend the reliable life of over 75 million feet of medium voltage underground distribution cable. Materials with superior safety and reliability performance have been introduced and are rapidly supplanting the venerable PMDMS, just as tree-retardant cross-linked polyethylene (TRXLPE) formulations replaced cross-linked polyethylene (XLPE) in North America. But for the cost conscious circuit owners such as those in developing economies, the low cost of PMDMS may be attractive. This paper introduces a reformulation of the venerable and inexpensive PMDMS and demonstrates a substantial performance improvement. Finally, all three commercially available technologies are considered in an ingredient-by-ingredient comparison.

## INTRODUCTION

Over twenty years have elapsed since the authors introduced the first commercially significant solid dielectric enhancement technology described in [1]. During those two decades, this first generation technology has proven itself as an important tool to enhance the reliability of aging infrastructure, saving circuit owners an estimated US\$1B of capital, which otherwise would have been spent on costly replacement. Incremental improvements during those two decades have aided in the widespread commercial acceptance of dielectric enhancement technology on at least four continents.

This paper focuses on the historical development of the rejuvenation chemistry and introduces a reformulation utilizing the best aspects of previous iterations. While the reformulated version of the old technology remains inferior to the improved class of materials introduced in 2006, the reformulation represents a significant improvement of the older generation of fluid. This improved version has potential applications in cost-sensitive developing economies, for projects where the required life extension is modest, and where the operating temperature of the cable is below 25°C.

## HISTORY

Figure 1 provides an overview of the development of the rejuvenation market. The very first injection technology was introduced in 1984 and involved the perpetual injection of acetophenone into power cables at Orange and Rockland Utilities [2]. This process was a technical success in that there were no post-treatment failures. The process was operationally burdensome and ultimately uneconomical, because the acetophenone (AP) was fugitive and reservoirs supplying fluid had to be replenished to maintain dielectric performance.

Five years later in 1989, a process Gary Vincent invented and described in [1] became the successor technology to acetophenone. This technology, which is referred to in this paper as 011a, included a hydrolysable and condensable

silane, phenylmethyl-dimethoxysilane or PMDMS. To facilitate the reaction of PMDMS, particularly the condensation step, a condensation catalyst titanium (IV) isopropoxide (or  $TiIP_4$ ) was included at 0.2%<sub>w</sub>.

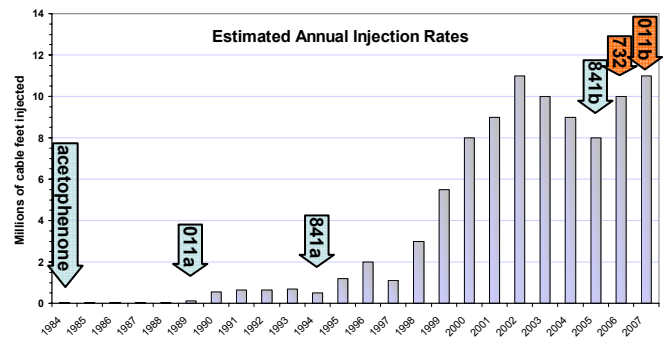


Figure 1. Estimated annual injection rates from [5] with key fluid developmental milestones.

While 011a enjoyed modest commercial success, there were an unacceptably high number of cases where post-injection failures occurred. It was those failures that drove the conception and development by Bertini and others described in [3], which resulted in the next advancement in 1994, referred to as 841a.

It was the greatly improved dielectric performance of the 841a technology, which drove the widespread commercial acceptance of the technology over the next decade. In 2002, it was discovered and described in [4] that in certain unusual circumstances it was possible for 841a fluid to corrode aluminum strands severely enough to cause failures. This corrosion problem with 841a drove a formulation modification, 841b, which was introduced in 2005.

In 2006 the authors of this paper, the inventors of both the 011a and 841a technologies, introduced an entirely new formulation of injection technology, coded as 732. That technology is described in [5], [6], [7], and [8] and is not the focus of this paper. However, the reader might reasonably wonder why the 011 and 841 technologies should be perfected, which is the focus of this paper, when the 732 technology is superior in every regard. 732 is ...

- **safer** with a flash point over 94°C higher than 841a/b;
- **faster** increasing post-injection dielectric strength 87-times quicker than 841a/b;
- **better** with life extension 3-times to 20-times that of 011a and 841a/b.

The answer lies in the economics. PMDMS, which is the basis of the 011 and 841 technologies, is a commodity silane

produced in large quantities for hundreds of applications. By contrast, the silanes utilized in the 732 technology are custom formulated to provide optimum rejuvenation performance. Even as the majority of circuit owners switch to 732 technology, the manufacturing volume of the specialty 732 silanes remain a small fraction of the production of PMDMS. High volumes in manufacturing result in lower prices. In developed economies the incremental cost of the 732 specialty chemicals is minor compared to the reliability and safety benefits. In developing economies such as Southeast Asia, South and Central America, and Africa, where the labor costs are low, material costs become a significant portion of the rejuvenation expense. Developing economies also have a higher tolerance for power interruptions. In short, for less demanding applications, which meet the criteria listed in Figure 2 and where lowest possible material cost is a factor, it is appropriate to consider the 011b technology.

Less Demanding Applications
Only a short life extension is required
Low operating temperatures (<25°C) in mesic (cool) soils
Preventative or proactive treatment on cables that have not recently failed

Figure 2. Criteria to define less demanding applications.

011b is the perfection of two decades of PMDMS research and field experience conceived and reduced to practice by the authors, who were also responsible for the conception and widespread adoption and use of 011a and 841a.

## INGREDIENT HISTORY

Figure 3 provides an ingredient summary of the commercially significant rejuvenation technologies employed over the last two decades.

Ingredient	AP	011a	841a	841b	011b	732
Acetophenone	100				~10	Yes
PhMeSi(OMe) <sub>2</sub>		99.8	70	~95	~90	
TiIP <sub>4</sub>		0.2	0.2	0.2		
Me <sub>3</sub> SiOMe			28.8	~5		
Tailored catalyst					Yes	Yes
Tailored silanes						Yes
UV package						Yes
PD package						Yes

Figure 3. Ingredient summary for all commercially significant rejuvenation fluids. Values are in weight percent.

## ACETOPHENONE

Acetophenone is the mother of all injection fluids. With an untarnished performance record, there are three reasons why

the approach did not survive. First, due to the fugitive nature of the non-reactive acetophenone, it was necessary to provide a continuous reservoir of fluid to the cable over its intended life. The labor costs for this perpetual maintenance were unpalatable. The second and related reason was the safety hazard associated with the fluid reservoirs and injection access points. Dead-front equipment had to be reclassified as “potentially energized”. That classification obviated many of the operational advantages of dead-front equipment. Finally, acetophenone suffers from a high freezing point preventing its use during at least portions of the year when temperatures dipped below 20°C.

## 011A

When 011a was introduced in 1989 all three of these problems were immediately solved. The 011a chemistry was very simple. The formulation included 99.8%<sub>w</sub> PMDMS (PhMeSi(OMe)<sub>2</sub> in Figure 3) with 0.2%<sub>w</sub> titanium (IV) isopropoxide (TiIP<sub>4</sub>), along with a trace amount of blue dye. The PMDMS includes two water-reactive methoxy groups (OMe), which react or hydrolyze with water available in the cable. After this first hydrolysis the methoxy groups are converted to hydroxyl groups (OH). This hydrolysis reaction occurs readily with or without the TiIP<sub>4</sub> catalyst. The next and most important reaction, however, does not proceed at an appreciable rate without the catalyst. This second reaction is called a condensation reaction, because a water molecule is created when two methoxy groups combine. This same condensation reaction is used for cross-linking in the manufacture of some cable insulation types. **If the treatment fluid exudes from the cable it can have no impact on dielectric performance.**

In [1], Gary Vincent demonstrated that PMDMS does not undergo appreciable condensation even after over 2000 hours at 25°C unless there is catalyst present. There was (and there remains) a problem between the TiIP<sub>4</sub> catalyst and the PMDMS, which would go unrecognized for about 18 years.

Figure 4 demonstrates the mismatch between the diffusion coefficients of PMDMS and TiIP<sub>4</sub>. The monomer PMDMS diffuses about 5.8-times faster than the catalyst, which PMDMS requires to undergo the critical condensation reaction. The consequence of this mismatch is that over a third of all the PMDMS injected never condenses, but rather is prematurely exuded from the insulation, providing no long-term performance benefit to the cable.

This loss has been measured in full-size cables and in model cables. Figure 5 provides snapshots of the concentration profile of 011a fluid over a 248 day period at accelerated thermal conditions of 60°C. This data was integrated as described in [7] and compared with simulated exudation as shown in Figure 6. The results demonstrated that 35% of the PMDMS exuded without condensing, because the catalyst was not able to keep pace with the faster diffusing PMDMS.

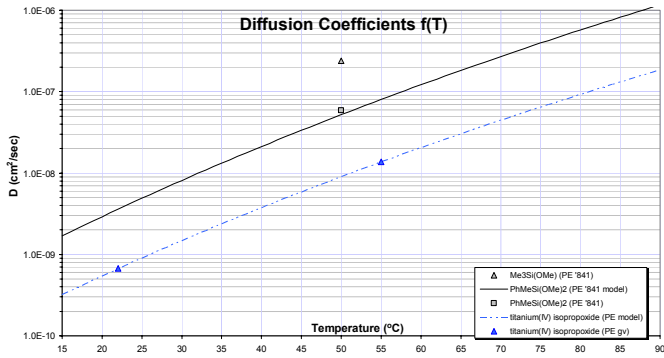


Figure 4. Diffusion coefficients as a function of temperature for 011a, 841a, and 841b technologies.

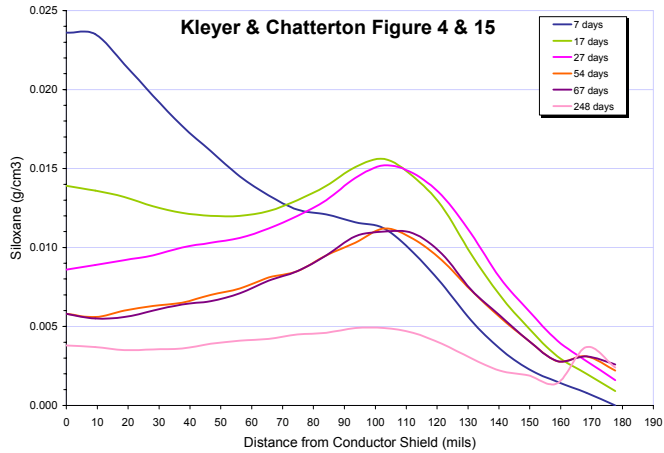


Figure 5. Micro-IR siloxane concentration profiles at various post-injection times for the 011a technology for a 1/0 cable immersed in 60°C water. Data from Figure 4 of [9] and Figure 15 of [10].

A second validation was recorded in one-sixth scale model cables. This exudation experiment was described in [11] and the experimental results are repeated in Figure 7. The horizontal line at 74.9%, labeled “MeOH loss”, shows the maximum (thermodynamically possible) performance, based upon the stoichiometry of the PMDMS and water reactions. The diamonds show the rapid exudation of PMDMS from the model cable in an anhydrous environment where there is no chance of condensation. In about 50 hours all of the PMDMS exudes from the model cable. When the same model cable is placed in water (triangles), hydrolysis and condensation occur, which dramatically slow the exudation. The exudation reaches a plateau near 45% of the originally supplied fluid weight. This 45% plateau represents a 39% retention inefficiency. After accounting for the unavoidable loss of methanol, 39% of the supplied fluid quickly exits the cable and depending on the cable operating temperature does not provide any reliability benefit beyond a few months to a year.

With benefit of hindsight, the choice of  $TiIP_4$  was far from optimum. It is a testament to the fundamentals of the

technology that, at least for non-demanding applications, 011a performed as well as it has.

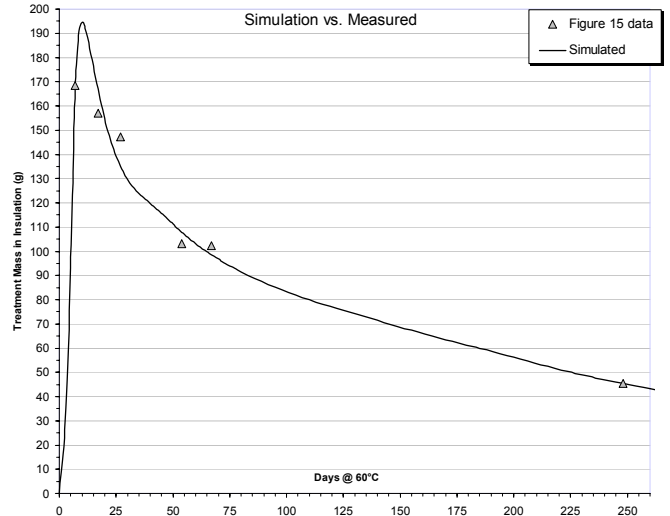


Figure 6. Integrated siloxane concentrations from figure 5 compared to simulated performance from [7].

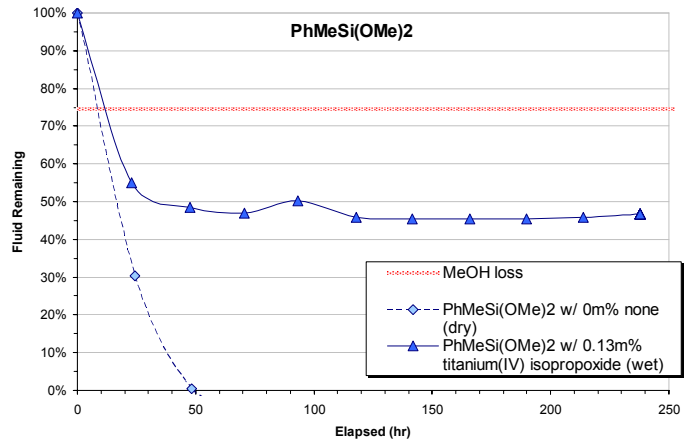


Figure 7. Exudation profile of 011a at 60°C in anhydrous and wet environment as described in [11].

### 841A

In 1994, Glen Bertini taught in [3] that a substantial improvement in dielectric enhancement could be realized by adding about 30%<sub>w</sub> of a new component. The new component was trimethylmethoxysilane ( $Me_3SiOMe$  or TMMS). This formulation is recorded in Figure 3. The impetus for this change was poor dielectric performance of 011a. Micro-IR studies of treated cables demonstrated a non-uniform penetration profile. An example of such a poor penetration profile was provided in [12] and is reproduced in Figure 8.

The cable cross-section is divided into equal slices and a profile of silane and siloxane concentration is taken at 3 o'clock, 6 o'clock, 9 o'clock and 12 o'clock. If the fluid were penetrating evenly, then the four profiles would be quite

similar. In fact, the penetration was inconsistent and less than 1%<sub>w</sub> at its maximum. Each of the 4 slices provides very different concentrations and at least one of the four profiles has essentially no silicone fluids present. Note that the results are negatively biased and were not corrected by the author, but of course, negative concentrations are not possible. All values should be adjusted upward by approximately 0.2%<sub>w</sub>.

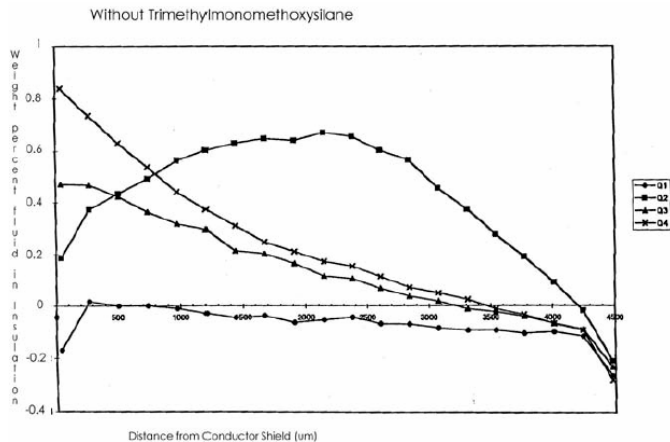


Figure 8. 011a asymmetrical penetration.

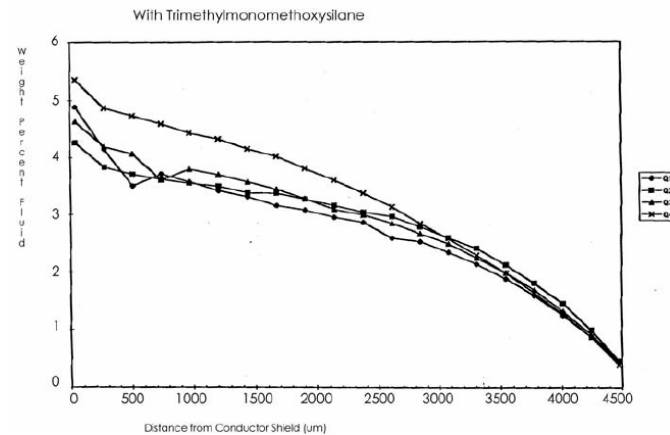


Figure 9. 841a symmetrical penetration profile.

Figure 9 is the same cable when treated with 841a. The addition of the TMMS at 30%<sub>w</sub> has a dramatic effect. Note that not only is the penetration more uniform, but the absolute values of the concentration are about 5 times higher.

The 841a modification of the formulation had a profoundly positive effect on the dielectric performance of cables, which were tested and have been documented in numerous publications including [3] and [9].

The catalyst mismatch, however, remained undetected and the introduction of the trimethylmethoxysilane exacerbated the problem. A review of Figure 4 shows that TMMS (the triangle) diffuses 26-times faster than the TiIP<sub>4</sub> catalyst, so virtually all of the TMMS exits the cable a few months after the injection. Of the small amount that does condense, most condenses to hexamethyldisiloxane, which is itself a fugitive

compound. The tiny amount, which condenses with PMDMS, serves to cap that oligomer, preventing elongation of the oligomer in at least one direction. This end-capping is counter productive to the goal of creating large non-fugitive oligomers.

With the benefit of hindsight the TMMS at 30%<sub>w</sub> had a profoundly positive impact on the performance of the base PMDMS, not because it was water reactive or condensable, but simply because it dried the cable with a process we have now come to call radial exclusion. Radial exclusion is a molecular thermodynamic process, which is beyond the scope of this paper, but will be described in [13].

There were (and there remain) two penalties imposed by the introduction of TMMS to facilitate the penetration of PMDMS into insulation polymer. TMMS is a very low boiling and low flashpoint material, which increases the vapor pressure, creates a flammability and explosion hazard (i.e. The flashpoint is -5.5°C from MSDS.), and under certain circumstances can contribute to the methanolic corrosion of aluminum strands as shown in [4] and [12]. It was this latter problem, which led to 841b, the only formulation in the history of injection, which was not developed by the authors.

### 841B

In 2005, as explained in [12] and [15], and as shown in Figure 3 and [14], the amount of TMMS was reduced almost six-fold to about 5%<sub>w</sub>. While it is beyond the scope of this paper, the performance compromise of this change, which according to [3] provides far from optimum dielectric performance, is unjustified. To wit,

*“For the purposes of the present invention, the amount of water reactive compound [TMMS] that is included in the fluid mixture is the least amount needed to reduce the asymmetric penetration front of the antitreeing agent [PMDMS] ... preferably in the range of about 70/30 [PMDMS/TMMS].”*

841b sacrifices the proven performance of 841a in order to increase the boiling point of the supplied mixture. The authors know of no published data, which demonstrates the dielectric performance of 841b. It is safe to assume that the performance of 841b lies somewhere between the performance of 011a and 841a, and since the TMMS was reduced six-fold; it likely performs closer to two-decade-old 011a.

In a future paper the authors will demonstrate the root cause of the methanolic corrosion, which apparently drove the 841b formulation change. We will also demonstrate that boiling is neither a sufficient or necessary condition, but rather is an accelerating factor. To limit the scope of this paper we are content to assume that the proposition put forth in [12] and [15] is correct and return to this subject at a later date.

## 011B

011b encompasses all of the lessons learned from two decades of experiment and experience. 011b uses the same low-cost, tried-and-true silane monomer (PMDMS) as used by 011a, 841a, and 841b. 011b makes two substitutions for the remaining two functional ingredients. The first substitution is acetophenone for TMMS and requires no compromises.

- **Safer** – the TMMS is the source of the low flash point of 841a/b technology and the serious safety implications flammability entails, as documented in [14].
- **Cheaper** – TMMS is considerably more expensive than acetophenone.
- **Better** – by all measures of performance, acetophenone excels in the short-term rejuvenation role. It also has a boiling point of 202°C, eliminating any concern raised by [12] and [15].

A more thorough explanation of the superior dielectric and thermodynamic performance of acetophenone will be provided in [13].

The second substitution corrects the greater than 33% exudation inefficiency of the TIPT catalyzed PMDMS. A proprietary catalyst package breathes new life (about 33% more new life) into the old technology invented by one of the authors over two decades ago and improved by the authors over a decade ago. A thorough description of this new catalyst technology is beyond the scope of this paper, but will be described in [16]. The proprietary 011b catalyst package is similar to that used in the advanced 732 formulation and constrains exudation inefficiency to less than 1%.

## SUMMARY

For applications that demand the highest levels of safety and reliability the most advanced cable rejuvenation technology should be utilized, namely 732. However, for a handful of cases including ...

- applications where only a decade of life are required,
- cables with low loads in cool (mesic) soils, and
- developing economies where low material cost trumps reliability, ...

... the 011b technology offers the same safety as the 732 technology, short-term performance superior to 011a, 841a, and 841b, and extended performance at least 33% superior to 011a, 841a, and 841b. The 011b fluid stays in the cable longer.

Both the 011b and the 732 technologies can be applied with the more advanced sustained pressure paradigm described in [5] with its improved safety and superior dielectric performance, or with the two-decade-old unstained approach. Circuit operators have the flexibility to deliver state-of-the-art chemical technology with either operational paradigm.

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## AUTHORS

Together, Mr. Bertini and Mr. Vincent hold over 50 patents with about one-third in the cable rejuvenation field. All of the silane rejuvenation technology in use for the last two decades was pioneered by this team. Mr. Vincent is a chemist and a member of the IEEE for over two decades and Mr. Bertini is a chemical engineer, a senior member of the IEEE, and a voting member of the ICC.