Polyencapsulated Dry Film Paint Preservative:
A Better Alternative

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Introduction:

Dry film preservatives in Paints have recently attracted lot of attention. There are two major issues, performance and toxicity. Performance is a critical property, which shows money's worth to a customer, but the related toxicity concerns of leached preservatives from the film are more alarming to everyone. A lot is being talked about and many efforts are made to ensure minimization of likely toxicity threats. The governing body which issues biocide product directives on usage of certain active substances in such formulations reviews both the aspects from time to time, as and how further data on toxicity of certain molecules is being made available. However, much needs to be thought and talked on this complex subject.

Many formulated products are available as dry film preservatives. All formulations are based on known and registered molecules, and each formulator supports his product with the data available on performance of formulation. There are formulations, such as those based on OIT, Diuron, Carbendazim as one set of products, which are most studied chemistries today; and other newer ones based on IPBC, Chlorothalonils, Zinc pyridinethiol-oxide complex, etc., and their combinations. Almost all formulators seem to offer almost identical percentage combinations of actives once a choice is made for doing the formulations. Carbendazim has been by far a major constituent of film preservatives.

In April 2004, carbendazim was shifted from Class III to Class II substance; this decision was based on the microbial/mutagenic studies related to carbendazim as a molecule (and not from its quantity emitted from the dry film of paints, or its estimate, to guide by) and apprehensions were expressed on its ill effects on masses. It has not been clarified whether and how the emitted quantities of carbendazim from the dry paint film are going to affect the mass population and to what extent. It is worth making a note that very large quantity of carbendazim is being used in pesticide formulations, especially for soft skin fruit crops, as compared to the quantum involved in preservative formulations. BPD now restricts its content usage as one of the components of dry film preservative to below 1000 ppm in final paint. It is feared that such a decision may lead to an unusual and multiple "Crisis of Confidence" for Paints sector to face. If the replacement of carbendazim is to be attempted from the available actives at hand, sufficient data is not available to guarantee performance and toxicity profile. Secondly the fear always exists that the story of carbendazim may get repeated for next molecule in use later. This situation forces the Biocide Industry to look for newer ways of formulations, which need to be applicable to all molecules and it is expected to open new technological advances.

A Few observations in the past:

It is common to find variation in the performance of dry film preservatives and such variation is acceptable too, but occasionally it reaches below-par level in tropical

countries. Unfortunately, when below-par performance is observed, there is no quantifying answer available to draw a concluding line why it occurred. All answers thereafter appear to be subjective, such as deterioration of film by microbial infestation after unusual weathering, which was said to be due to high rainfall, persistent humidity or moisture and sunlight, weaker film, poor film thickness, and, a variety of answers, which are related to both, formulation of paints and application methods of paints. None of them are arguably absurd, but as said above, since these appear to be subjective in absence of quantification criteria, they may become unacceptable to many.

One of the remedies, or a proactive solution, helplessly suggested under such conditions by a biocide formulator is to increase the dosage of dry film preservative.

What is subtly suggested by increase in dosage?

1. There could be significant loss by migration/leach out (or emission) of preservative from dry film, (which is due to the assigned reasons such as excessive solubilization due to weathering, rainfall, humidity, moisture, weaker porous film**;** all of them leading to depletion of actives), which is expected to get compensated by increased dosage.

2. There could be insufficient presence/ unequal distribution of preservative in the dry film (which is shown by assigned reasons, such as, high film thickness and presence of gradient of distribution of preservative across this thickness, imbalanced paint formulation, variation due to paint application methods, and similar reasons) and the increase of dosage is expected to compensate for such non-uniformity.

What needs to be understood?

Most dry film preservatives are formulated products with multiple numbers of active molecules, and therefore, the picture as above is more complicated than imagined. Apart from the quantum of presence of the preservative in the dry film, and whether it is sufficient or not, which molecule from the combination gets depleted more and which molecule is distributed in what way in the dry film are more critical and decisive factors. Therefore, it is better to assume that both decide the performance of dry film.

Thus minimum sufficiency of preservative in dry film is one aspect, whereas whether it is distributed and thereafter retained in the film in the same ratio of components or not, as formulated, is another issue deciding the long-term performance, and both need to be studied.

Some missing links in the subject:

Biocide Industry so far has not systematically addressed one important topic to debate and study.

It is whether the dry film preservatives are expected to perform by way of some kind of gradual surface leach-out, i.e., by way of freshening of anti-microbial activity at the surface of the film, or by way of their uniform presence in the (top-most layer…?…) of dry film, creating a resistance, or barrier to microbial attack. Leach-out (or emission) is an observation from the reality. Most often, it seems to have been assumed that 'leach-out from film surface' is a way of activation of surface to resist attack from microbes. If that assumption is to be carried forward as a modality of action, what needed to have been studied and then defined are:

(a) Ideal rate of leach out of each component, w.r.t. film thickness
(b) Combined rate of leach-out,
(c) Effect of leach-out of one component on 'preservative balance', and
(d) Leach-out rate vs. performance.

The data as above becomes essential, based on which formulation-optimization could be carried out. Also required is the determination of minimum threshold concentration of each molecule for the on-set of microbial deterioration after leach out, if 'leaching' is assumed as a mode of action.

Above data is required at least for an ideal system, if not for practical cases to get very explicit understanding on such biocides. It is difficult to derive the same. Since 'leach out of molecules from the formulated preservatives' in dry film is real life situation for some reasons, (in spite that it is unregulated), Biocide Industry appears to have accepted it, as if it is 'desirable way' of getting the performance. How far and how much 'leaching' is permissible needs to be probed too.

The immediate thought thereafter is, 'controlling unregulated leach out to minimum' may offer better environment safety and performance too. This presents a new direction of research on biocides.

Points of initiation of present work:

As said, the degree of leaching-out or emission of actives and thereafter deterioration of film by microbial attack seems to vary. It needs to be understood that certain components of dry film preservative formulations, as also paint formulations, seem to increases "the solubility" of the active molecules of preservatives. These are:

1. Surface active agents/emulsifiers
2. Coalescing solvents
3. Other functional chemicals used to derive specific properties, such as flow, leveling of film, removal of air-bubbles, etc., all of which are again SAAs.

Further, most dry film preservatives are prepared as aqueous dispersions using sufficiently large quantities of SAA in formulations. Use of SAA to get stable dispersion often leads to increased (pseudo-) solubility of otherwise difficult to solubilize active molecules. This needs to be accepted as a threat to performance of such formulations, as aqueous dispersions.

It is also necessary to find out what happens to SAA when film dries, how and the extent to which SAA can lead to micro-canalizing while the film goes to dry state from aqueous phase, whether SAA are first to show migration to surface while film dries and finally how soon from the dry film by heavy on-slaught of rain. Further topics to debate and study are, whether coalescing solvents help the process of solubilising such SAA-coated active molecules of preservatives, or they suppress it by de-stripping SAA from the grains of active substances**;** how SAA may increase the porosity of the film, and thereafter increase the chances of microbial attack on the dry film surface through created voids. No study has been reported so far to get answers, though this author in the context of Hygiene Coatings had raised these issues. But by virtue of these arguments, it becomes clear that one has to work to avoid the excessive usage of SAA while formulating a dry film preservative, which might resolve most of these issues.

Use of polymeric SAA, which may combine with polymer matrix of paints, is one solution (1) and it is greatly advocated in recent times, as the migration of such SAA gets arrested.

Secondly, it is a worth to note that 'uniform presence of dry film preservative in the dried paint film' is far bigger subject than it appears. Unfortunately, this subject also has remained un-addressed so far from Biocide Industry.

Basic question: What is 'Uniform Presence'?

There are two points to question**:**

1. Whether there is a likelihood of existence of distribution gradient of 'dry film preservative' across the film thickness, or is it that its presence is uniform across the film thickness? (Refer to **Fig. IA and I B**).

Generally it is assumed and claimed that the dry film preservative is almost uniformly available across the film thickness. Whether it is so or not cannot be easily detected.

Two questions arise. If a gradient exists, what is the criterion of determining efficacy of the preservative? If the presence of the preservative is uniform, what is the mechanism of protection? (what is mode of action?)

In relative terms, the answers to above are somewhat easier to find, if a preservatives has single active component.

2. As said earlier, almost all dry film preservatives are formulated from multi-components, such as anti-algal, anti-fungal, anti-bacterial speciality molecules. A few molecules have multiple functions. Their ratio in the formulations is apparently fixed and most formulators use the same ratio (but adopt different ways to get stable dispersions). It is assumed under normal conditions, that the same ratio of components, as formulated, will uniformly exist in the dry film, to give each site of dry film the same protection value, and it will be so, irrespective of mode of action of preservative.

Rather, dry film preservative formulations having multiple components are made with these assumptions, and it is expected to show always a uniform distribution in dry film.

There is no particular reason why each molecule of the preservative-composition would not get randomly distributed in the film, instead of remaining in the same ratio 'in associative manner' at all times in the matrix of dry film. A non-uniform distribution of components will definitely lead to variation of the performance of the dry film, as a few patches of dry film will not have sufficient protection from the microbial attack due to absence of one or more active molecules in that zone. (Refer to **Fig. IIA** and **IIB**).

2.a) More specifically, what is the meaning of 'the synergy' that such multi-component blend of a dry film preservative creates, if this mixture is least likely to retain 'uniform associative ratio of components' in the film, as added? Biocide Industry very cautiously or rarely uses the word 'Synergy' today, due to many other issues arising out of combination of actives in a formulation, and due to BPDs. Nevertheless, these need to be addressed in future with proper data.

Synergy may falsely indicate today to many that the present ratio of each molecule in the preservative formulation is perfectly optimized, but once again, this aspect has not been confirmed in the past.

Also please note that “Synergy” seems to exist in Nature, it could be perceived and let us accept its necessity when one derives a formulation. Interestingly, a report on ‘Synergy Index of Biocides’ exists (2) but it may require further refinement in light of what is said above.

Brown: Substrate **Blue: Dry film**

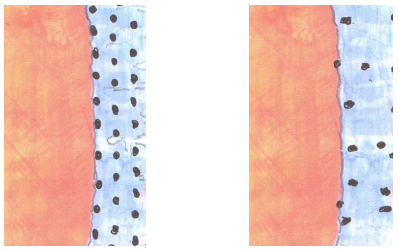


Fig I A **Fig I B**

Uniform and non-uniform distribution of single preservative molecule in dry film

Brown: Substrate **Blue: Dry film**

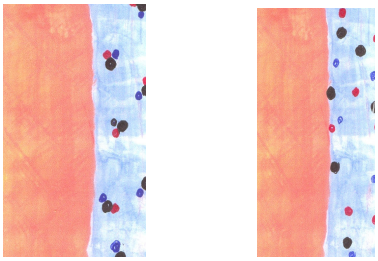


Fig. II A **Fig II B**

Uniform and non-uniform distribution of multi-components preserve. in dry film

2.b) Further, Brownian Dynamism is absent in highly viscous materials as also in a state leading to dry film, which is responsible to create and maintain uniformity of a mixture in liquid state. Therefore, how can one assure that the same ratio of formulation of actives will get retained till the film dries? (Till phase difference occurs). The individual active molecules can randomly disperse according to their surface properties and remain anywhere in the film.

Secondly, why should one assume now, that the present ratio of such molecules in multi-components preservative formulation is a right ratio, and that, no component of it is in excess above the optimum requirement? In addition, there are likely economic implications, sometimes of excessive usages of some components, in order to get the best average results, apart from toxicity concerns, and both are not studied so far.

These questions are applicable for all compositions of dry film preservatives, and not related to those popularly based on OIT, carbendazim and diuron. In fact these questions are raised for all ‘synergy systems’ (Synergy is ideally defined later) and also for all formulations, where there is likely existence of phase difference from liquid to solid, and not for paints alone, like adhesives, paper boards etc., as individual system in operation.

3. Once the knowledge about these aspects is available, the dry film preservatives will stand to create revolution. These will meet the environment safety norms.

4. Such doubts do not arise today for wet-state preservatives, since Brownian motions in a liquid will always create a dynamic uniformity of composition of preservative, even if wet-state preservative is a multi-component blend. For pasty or viscous compositions, this uniformity may not be completely achievable, and therefore, wet state preservatives will also need to be reviewed from the angle of ‘synergy’ and will be a subject of review in future.

The questions raised above suggested a change in formulation-technique whereupon the present work initiated.

Objectives of the work:
1. To ensure a mechanism of uniform presence of each component of such preservative in dry film, and

2. To minimize the leach out.

Both were viewed as dependent on each other, which was a bold assumption.

Further objective:

"Synergy" and what could be the ideal synergistic combination (which means optimization of content of each molecule in presence of each other, from all angles, to form an ideal workable system) was listed under the next programme of study. This study is not over.

Assumptions:

Two assumptions were made at the beginning of the work.

a) The uniformity of preservative-presence gets disturbed and the film deteriorates, and
b) There is uncontrolled emission of actives from the dry film and the film deteriorates.

These assumptions were, in the first place, contradicting the present promotion-principles of dry film preservatives. Biocide Industry claimed other way round to promote the use of such preservatives for over a decade in the past and which the Paint Industry accepted. The new thought was likely to make the previous claims on such formulations as worthless! However, there is no suggestion of this kind while reporting this work.

Available Direction for the work on dry film preservative:

The thoughts as above finally led to Encapsulation of the active molecules in a polymer matrix and deciding not to use monomeric surface-active agents while formulating dispersion, as a new way of initiating a formulation of a dry film preservative. It was found to give great results**.** The word 'Polyencapsulation' is introduced here to denote the process of delivery of an active substance, or the combination of more actives through a polymer, in a definite manner and in summarization of this process**.** Use of polymeric surfactants of low surface activity along with other polymeric substances as modifiers is made as ' composite polymer base' for carrying out encapsulation and finally achieving stable aqueous dispersions.

The results obtained from this approach are now being reported in short**.**

This work is being termed as 'Application Research on Delivery System of Preservatives'.

Microencapsulation has application across a very broad range of industries, e.g. the first applications provided the print industry with the ability to provide copies without carbon paper! Further, enhanced encapsulation techniques are recently commercialized (3, 4, 5, 6) in the attempt to make drug-delivery in health-care use very specific to location of action, optimize the dosage of drug and reduce the unwanted after effects. By following encapsulation, pharma industry could handle certain labile preparations with extra-ordinary ease too. Microencapsulation is a process by which very tiny droplets or particles of liquid or solid material are surrounded or coated with a

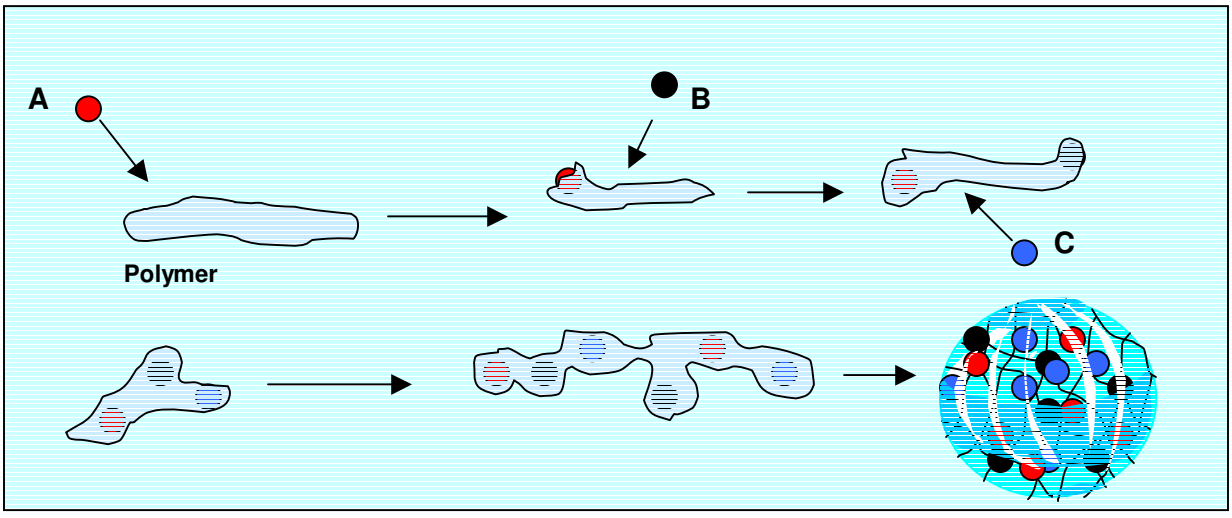
continuous film of (polymeric) material. These micro-capsules have a number of benefits such as converting liquids to solids, keeping reactive compounds separate from others, providing environmental protection, improved material handling properties, etc., The active ingredient-capsule is further protected against:

- high temperatures
- the effects of weathering
- pressure
- water
- degradation in air, etc.,

Table I: Typical properties of Encapsulated materials.

Characteristic	Benefits for user
Solubility in water	Can be suitably changed. Both dry powder and paste forms are possible, micro-capsule can be wet processed without solubilising the materials
Temperature	Can protect actives from evaporation, or early decomposition, able to survive exposure to high temperatures
Release mechanism	Active can be targeted to specific location for release
Particle size	From a few cells to hundreds of cell, micronized powder can be used, non-flying, non-dusting characteristics could be built.
Oxidation	Can reduce oxidative degradation, prolonging shelf life.
Performance under pressure	Release mechanism can be related to, or by fracture. The materials can withstand high pressures and shear force
UV protection	Natural UV filter can be built.

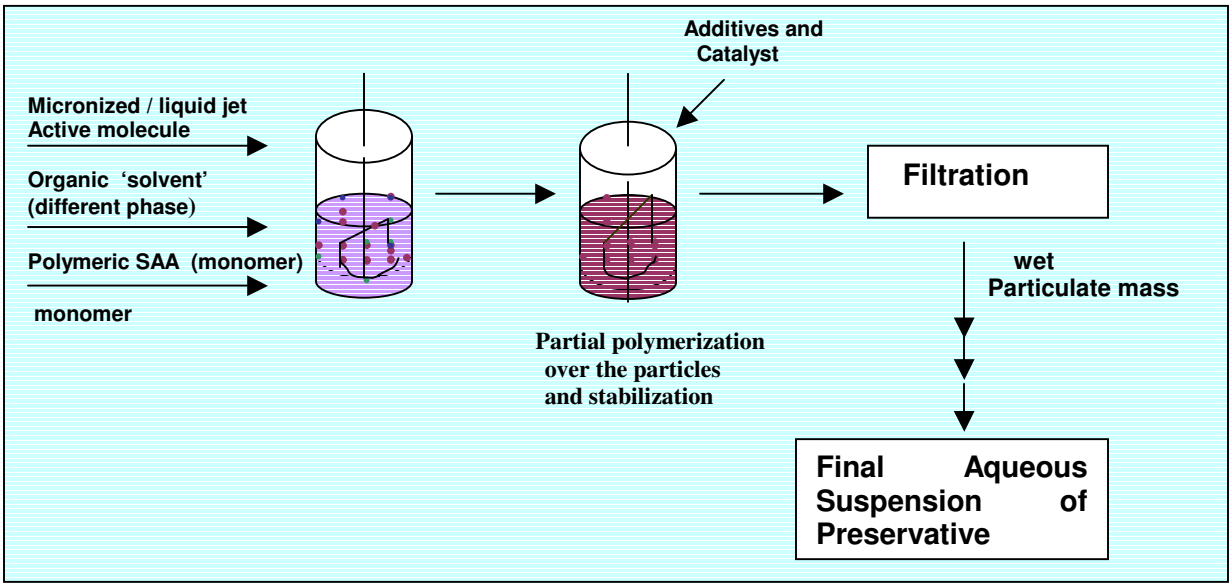
Principal of the encapsulation process: schematically shown in Fig. III (7)



(In Fig III above, a micro-particle is shown to enter a polymer matrix, followed by another and a micro-bead gets formed. Several micro-beads can be accommodated in one larger "enclosure" of the polymer, forming a capsule. These capsules suspended in aqueous medium can then be lowered into the system. Polymer can be chosen in such a way that it can exert an electrostatic orientation across its chain length in aqueous phase and thereby can suspend itself. It could be a polymeric SAA with mild surface activity. A self-suspension of such polymer-enclosed capsules in aqueous

medium may appear either as a stable dispersion or as a paste. This principle was used in encapsulation reported here. The choice of polymeric substances was crucial.)

Schematic Manufacturing Process is shown in **Fig. IV** (One of the two standardized processes)



Further details on the actual processes are not disclosed here.

The work now being reported is also being called as a step towards **'Value Enhancement of Actives'**

The encapsulated preservatives so obtained showed good stability as aqueous dispersion, have workable flow and consistency. These show no appreciable change in the rheology on storage at ambient temperatures. All of them are compatible with most paint systems, at the pH range 3.5 to10.5. The pH of formulations is in the range 6 to 8, and most often it is around neutral. No particular odour is observed.

Results:

The detailed discussion on the results is restricted, as it forms a separate subject by itself. It will be presented along with the results related to other dry film preservative systems.

The microbial performance study (relative performance) of the dry film preservatives with almost identical composition and at identical dosage (1.5 % w/w of wet 40% pvc paint) was carried out. Commercially available conventional dry film preservative was a reference material to the Polyencapsulated dry film preservative. In this study, both systems were subjected to leach-outs by the method suggested earlier (8), and microbial studies were performed thereafter for an extended period in the same manner. Another set of study was after artificial weathering. The weathering at Florida site was also carried out.

What was the degree of leach out of the active molecules by above method (8) from the film containing preservative was not known in the past, as a method to determine such data is unknown. 'A stagnant leach out in a water column' has been devised now as a new method to

explore an indicative leaching behavior of encapsulated preservative vs. non-encapsulated one from the respective dry films It gave (statistical) average leach outs of respective preservatives. The details about this method will be presented along with full details on the study. This method is not a true picture of dynamism involved in real life leach out by weathering and heavy rain. However, the consistent results from stagnant study as above are indicators of slightly (by 0.2-1.4%) lower leach-out as a combined percentage from polyencapsulated preservatives, as compared to leach out of actives from other preservatives. This pattern was observed irrespective of film thickness. It was a significant observation. Perhaps, stagnated leach-out rate and dynamic leach-out rate would differ, but the pattern is expected to remain the same.

In the end, the microbial study suggested that polyencpsulated dry film preservative has fared very well to retain the structure of the film without algal and fungal growth. The distinguishing difference between the preservative-panels was noticed by the least roughness and black spotting on paint film of polyencapsulated preservative, when the laboratory inoculations on freely suspended films and panels were discontinued, and the panels were left to follow natural weather conditions for the further period of two months thereafter.

One question is always raised, what is the ideal dosage of dry film preservative? Can this answer be dependent on the formulation of the preservative alone? Can one suggest a definite dosage? No answer is available, as most depends on paint formulation, and subjectivity mentioned at the beginning of this text seems to continue. However polyencapsulated preservative, in general, is making a difference in performance, as found from the relative study, where as much quantification as possible was attempted for giving performance rating.

How to verify whether Polyencapsulation really occurred?

This question was most important in this work, as every step of this work had presumed that one can 'bind' the three actives together and therefore, their ratio, as added, could be the same at any location in the dry film. It may probably create the 'synergy' by such uniformity of presence.

In order to confirm this, cryo-TEM (transmission electron microscopy) were carried out (9).

cryo-TEM is a tool to investigate the assembly, regulation and orientation of macromolecules and micromolecules in a complex aqueous phase by electron transmission microscopy. It allows visualization of delicate assembly of Amphiphilics and macromolecules in aqueous phase.

Amphiphilics are defined as surfactants, water, polymer etc, and their combinations. The solids could be any active particle, enzyme, extenders etc.,

Applicable to	**:** Particle size: 5 to 500 nm
Recording as	**:** Thin aqueous film
Structural picture	**:** Brownian movements arrested at temp of liquid nitrogen or In dried state, if permissible to dry.

The two samples were Microcheck MZ 33 and Sample A. Sample A is said to be a reference material in this study, which is another commercially known dry film preservative from a biocide manufacturer, and was chosen to compare the results.

Following techniques were used for microscopy.

1. Transmission recording using Bright Field

2. Cross Polars
3. DIC (differential interference contrast)
4. SEM (scanning electron microscopy)

The details on sample preparation for recordings are available on request**.**

1. In Summary, the Sample A (reference sample) showed that it has several crystalline rods or needle shaped particles along with many fine particles randomly placed, and they undergo Brownian motion and are carried along with the medium, they have no particular compositional consistency or togetherness with each other.

2. Whereas in the sample of Microcheck MZ 33, the individual fine particles, whether needles or crystals, are almost absent, but aggregates appear as large mass consisting of agglomerated crystalline solids, both needles and crystals, held together. (Association of solids).

3. In order to re-confirm this and get further clarity on this, SEM recording was done. The dried sample SEM recording confirmed the presence of similar agglomerates in Microcheck MZ 33, which is absent in Sample A. The associated particles are actually sol gels and micron gauge meter could not detect a large crust of hard particles of higher size, though they appear as if these are having higher particle size than 10 microns.

4. The encapsulation and agglomeration in MZ 33 sample results into the particles in the sample of MZ 33 not being carried around in surrounding water, which was used for dilution, by Brownian motion of individual molecules. This association in MZ 33 could be clearly seen, by way of comparison, in the SEM (SEI) recording in the dried state of both the samples, thus confirming successful polyencapsulation.

   (Microcheck MZ 33 is a registered product of MELZER)

The recordings of cryo-TEM are enclosed as miniature images. Please note, cryo-TEM study or other tool may not be possible for paints in order to locate the preservative in dry film.

Conclusions and Remarks:

Though polyencapsulated preservatives have shown good result of dry film performance, what is the mode of action of polyencapsulated preservatives is still a subject open for debate and study hereafter. If leachability is assumed as the only method of activation of surface to resist microbial growth, there is no conclusive evidence for its acceptance from above experimental data of stagnated leach out study. Therefore, the uniform presence of preservative components is still an indicative mode of action (forming an uniform barrier) for preservative to be efficient to perform. The argument advanced in support of the same is as under**:**

'Polyencapsulated' preservative is not a hard crust of molecular composition in a polymer, in which actives of preservatives are so deeply embedded that they remain permanently in that form. Polyencapsulation becomes a delivery method of active molecules, as actives are held through association with polymer. A force exerted by encapsulating polymer binds the actives together through its polarity points and this composition is loaded in the paint by a simple post-manufacturing stir-up. In all probability, the preservative composition remains in encapsulated

form till the phase difference in paint starts occurring. There is no particular method to seek evidence of this happening as on today. The phase change actually starts at brushing, spraying like application methods (both have energy in-put) and completes at the drying point of paint. Since the polymer chain is long, on which the active molecules are bound by associative forces, the uniform presence of active molecules of preservative in dry film across its film thickness, is most likely to be maintained. It happens due to two reasons, by stereo chemical effects (due to long chain of the encapsulating polymer) as also by its partial locking with paint polymer. It will be wrong to presume that individual molecules in polyencapsulated form are so deeply embedded or surrounded by the encapsulating polymer that they cannot get released (emission by leaching) for actions, as is a first impression of the user. If that were to be the case and accepted as likely phenomenon, then by virtue of the same arguments, one has to accept that the active molecules of most preservative would not have been available for normal leach out, whereby preservative performance could not have been expected, once these get embedded in polymer matrix of paint too. (Please note, polymer matrix of paints is definitely tougher than encapsulating polymer, whereby paint withstands to the hardship that it suffers. If such tough polymer were to 'embed' the actives of preservative, the leach out would not have been noticed under normal conditions, as it happens in most cases.) The point therefore is, polyencapsulation does not completely arrest the leach out of actives (please refer to 'Stagnated Leach out Tests'), but it is most likely to inhibit it**;** it basically helps to deliver the preservative composition in the paint uniformly and retains it as uniformly as one expects it to, till film dries**;** and that is the function and success of encapsulation.

Therefore, 'a uniform presence of active molecules in dry film as a barrier' is a most likely reason, and not 'leaching', which is responsible for the performance of such preservative. It is however not a conclusion. (In spite of lower leach-out, the performance of polyencapsulated DFP was better)

Algae require no particular surface situation to grow and it is not uncommon to see the algal growth occurring on surface like glass too. For preventing algal growth, therefore, it is generally presumed that preservative has to remain on the outermost surface. This encourages leachability theory as a method of action of dry film preservatives to prevent algal deterioration. Why polyencapsulated preservative showed sufficient resistance to algal growth is therefore a relevant question from the view of leachability theory. Perhaps, what needs to be studied is the transition point of surface growth to hard growth with respect to nature of algaecide as well as other properties of the algaecide molecules and their role in maintaining surface activation. In this particular composition, the presence of OIT, which inhibits algae, which is partially soluble in water and easily leachable as liquid, might have helped to get the best balancing properties and acted as a synergizer to other algaecide present in the formulation. (Also pl refer to solubility of each component)

The concept of 'Synergy from a Combination' may probably take a new orientation hereafter, once polyencapsulation of active blends and the resultant activity is well studied. There will be acceptance to the word "SYNERGY". This is most important development, as encapsulated actives and their arrested leachability will force the governing bodies responsible for issuing BPDs now to have re-look at the present BPDs as also to the synergy.

Another relevant topic is to work upon the encapsulation systems for solvent based formulations of preservatives. A need of dry film preservative with anti-mold properties is well underlined for automotive coatings**;** a few of them are oven-dried paints, whereas self-curing 2K systems are becoming very popular. Both require appropriate dosage of dry film preservative. Corrosion

control coatings also require dry film preservatives to avoid microbe-induced corrosion and marine coatings are already using film preservative as anti-foulants, which are tin-free.

Biodegradation of encapsulated preservative systems is an area, which may be studied in future for understanding and exploring the different aspects related to individual active molecule in relation to the combination, but it may not show significant variation from the present status. This is so, since as said above, 'Polyencapsulation' is an intermediate status of active molecules till delivery point and not a permanent one to alter the molecular properties, like biodegradability. There may not be any significant alteration in rate of biodegradation of actives.

Finally, to summarize, it certainly promises that 'polyencapsulation of biocides' offers better and safer route and in future, it will be preferred mode of delivery of biocides in almost all systems. This will shift the focus from searching new and safer molecules to the effective use of known molecules. It will be done by way of carrying out more innovative formulations, wherein their usage will be to minimum effective concentrations. A newer concept of 'synergy from the combination' will emerge and get firmly established. It will lead to a change in the thoughts related to BPDs, and all these together will create newer symbols in safety paradigm in this field.

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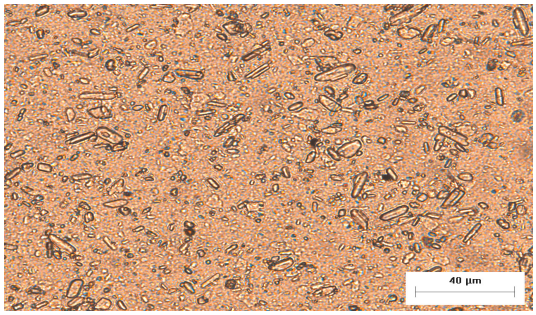
Annexure I:

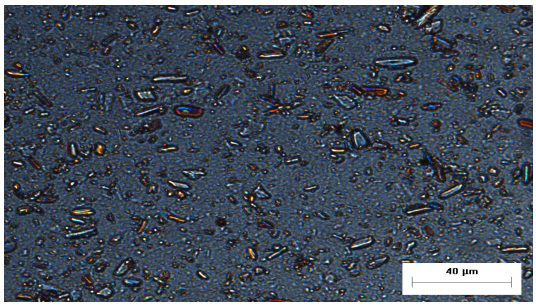
cryo-TEM RECORDS:

Bright field Recording: Conventional Formulation:
Shows random distribution of actives



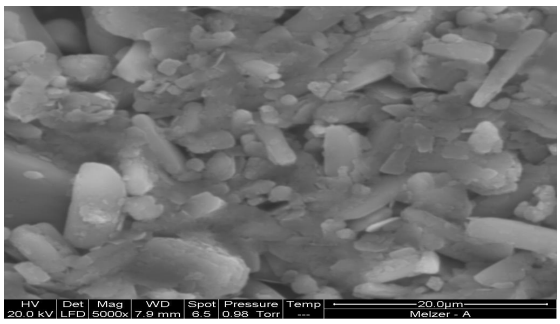
SAMPLE -A

DIC Recording of Conventional Formulation:
Shows random distribution of actives



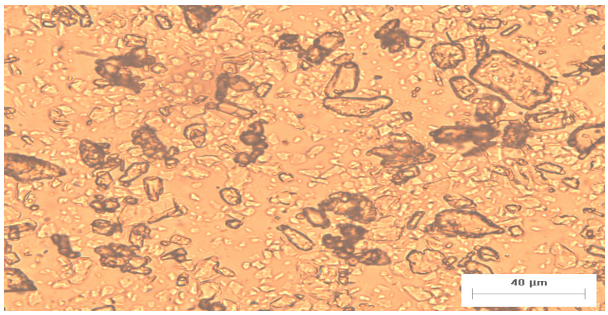
SAMPLE -A

SEM Recording of Conventional Formulation:
Shows individual molecules



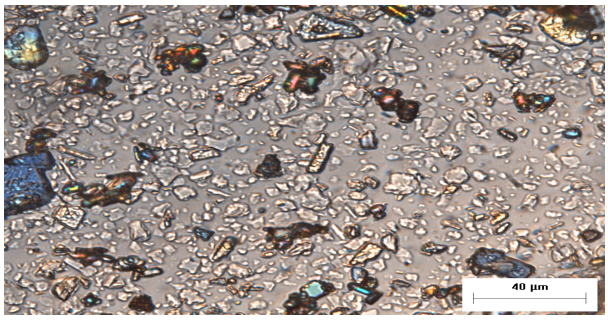
SAMPLE -A

Bright Field Recording: NEW Formulation:
Shows "Association of molecules"



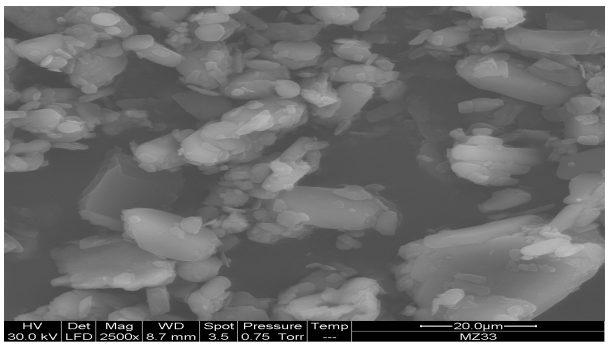
Microcheck MZ 33

DIC Recording of NEW Formulation :
Shows "Association of molecules"



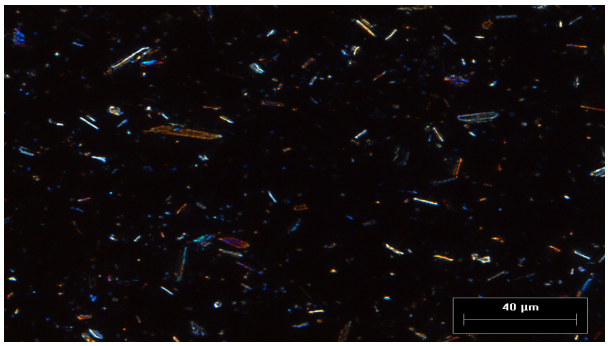
Microcheck MZ 33

SEM Recording : NEW Formulation :
Shows "Associated molecules"



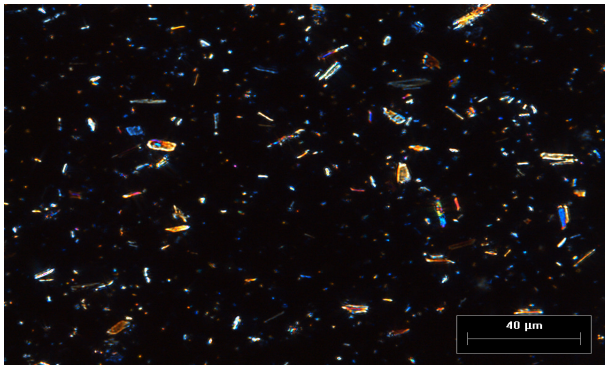
Microcheck MZ 33

Cross polar Recording: Conventional Formulation :
Shows more individual molecules



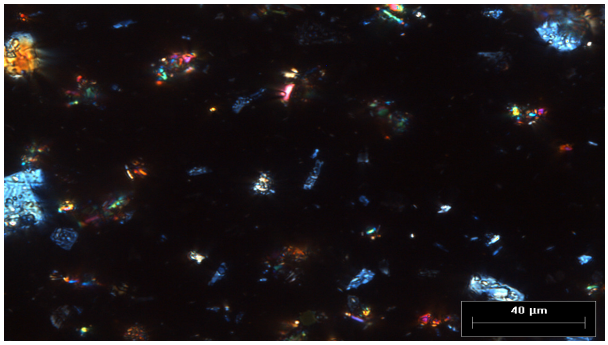
SAMPLE -A

Cross Polar Recording: Conventional Formulation:
Shows more individual molecules



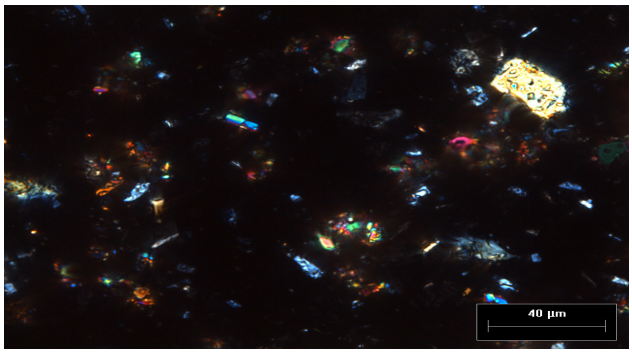
SAMPLE -A

Cross Polar Recording: NEW Formulation:
Shows "Encapsulated Molecules"



Microcheck MZ 33

Cross Polar Recording: NEW Formulation:
Shows "Encapsulated Molecules"



Microcheck MZ 33