

Dry Film Preservatives Mis-conceptions and myths

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"Biocides and Dry-Film Preservatives are an integral part of the Architectural Coatings landscape, and assume a greater significance in India, given the large share of this segment, the tropical climate as also the qualitative increase in coatings and the need for their longer life. There are varying perspectives and theories on the technology and regulations surrounding this. We, at Paintindia, intend to bring to the Industry varied and diverse views from credible sources, and allow the Industry to form its own opinions and judgements on the same. While Paintindia will always filter and verify the sources and content, the inherently controversial and subjective nature of the subject means that there will always be contrarian views on the same."

WHILE taking critical review of Biocides especially of Dry Film Preservatives (DFM) used in Paints, it seems that Biocide Industry has loaded in the user Paint Industry, a few myths too from long past, not limiting to true technical inputs, to sell such preservatives. It is unfortunate that this has been continuing further from time to time as per changing contexts. Thus, there are newer myths today. Those seem to have originated each time from the newly propagated mis-conceptions. The mis-conceptions in turn seem to have originated from certain vague claims on performance of such preservatives. The claims seem to be made with the aim to hold a competitive edge in market, to impress upon a user and for him to purchase such DFP preferentially. Thus, most users were driven by such myths and are now also getting driven too. It is therefore necessary to learn from introspective analysis.

To begin with, let us first see the claims which ruled for about three decades till about 2003-05:

1. Dry film preservative as a dispersion formulated by using multiple active ingredients, which ingredients when chosen in certain ratio, when added at the stipulated dosage in paints gets uniformly distributed in Paints on

blending into paint, and give excellent results of Dry Paint Film (There are two claims in this.)

2. So the added DFP also remains uniformly present in dry film of paints, was implied, which later became a claim by default.

The DFPs are actually formulated even today with such assumptions and expectations in mind. The dosage of such DFP was empirically found out, but occasionally random recommendations are being done to increase it if the film-performance is found to be low. Where does a DFP go, whether it remains mostly on the surface or it sinks to the bottom part of the dry film, and in what proportion such distribution occurs when the paint dries to form a film, are still unknown. But the user always thought that DFP remains uniformly present in the dry film as was being told to him, which was myth but was out of an ideal expectation. Later the stand on this picturization was slightly changed and DFP was being said to be available more at the surface of the dry film, whereby it became easy for a biocide-seller to provide an answer why leaching of the DFPs occurs without going into details of the subject. Biocide Industry continued with this myth too for a few more years.

are three active ingredients in many such DFPs, the meaning of the claim on "Uniform Distribution" of DFP gets further challenged. It is hardly possible that all three component-ingredients, each having its specific functionality, would remain uniformly present in dry film in identical ratio on entire surface of dry film when paint dries. The observation from the actual usage reported the microbial growth (algal or fungal) having occurred in patches and not on entire surface. It therefore appears that Biocide Industry sold DFPs by a wishful claim on uniform presence of the components of DFP in the film, and this claim continued for a couple of decades.

A nice picture was apparently provided to the users to support such claim. (which continues even today). "The degree of uniformity of the dispersion", as formulated DFP (having in it multiple active ingredients), became an indicator of a performing product! Buyers started thinking that very stable, non-settling type dispersion, not even requiring thorough stir-up before using and also requiring minimal stir up after dosing it in paints as ideal. It is true that a good dispersion as DFP offers to a customer, lots of convenience of handling it, and also can get quickly mixed in wet paints due to Brownian movement of the components in liquid state of paint. However, in spite of

having such stability, problems of patchy growth on dry film continued. It never occurred to a user that three active components in such dispersion also would get randomly distributed in the film, as the paint would dry. Therefore, it appears that helplessness to find the real solution towards ensuring 'Uniform Presence of the active components of the DFP in film' led to the mis-conception of stable dispersion as being ideal DFP.

Biocide manufacturers started recommending increased dosage of DFP as a ready solution, whenever the observed performance of dry paint was inferior.

In the meanwhile, another view was advanced and which continues even today. It was propagated that film performance decreases, especially in tropical countries, due to exposure of paint film to bright sunlight leading to excessive uncontrolled weathering of the dry film. Further, film-deterioration was said to be getting accelerated by frequent and unpredicted changes in humidity and temperature, or the cyclic repetitions of such changes, as also due to high level of dust and high rain-fall. On account of all of these factors, it was claimed that leaching of the components of DFP from the so-weathered film was getting pronounced and hence the poor performance. These claims might not be wrong but lacked quantification. These however got accepted by Paint Industry in spite of the fact that these have been challengeable topics by scientific logic of scientific world. Such talk introduced another major myth. Everyone in paint industry thereafter started talking on 'requirement of doing study over a couple years by subjecting the paint film containing DFP to weathering' for knowing the likely performance of the paint containing such DFP. The need for conducting such a study soon became a pre-condition for accepting a DFP, instead of going by the analysis on the appropriateness of the DFPs at least theoretically. Further it so happened that a few in paint industry started assuming and believing that a DFP promotes uncertain weathering of the dry film! Thus, another myth took firm position. It hardly gets accepted even today that outdoor weathering study on dry film cannot be conducted beyond a short time if the paint is not dosed with DFP!

Frankly speaking, the global paint industry has been spending year on year huge money to design better paints, with the focus kept on achieving better weathering-resistance of dry film. That further means, achieving film formation having excellent wet-rub resistance, resistance towards moisture penetration, ascertaining further the absence or minimization of pin-hole-porosity, its right balance on hardness and flexibility, etc., So the film characteristics get well-tested for ensuring film integrity over a number of years of performance against the exposure of paints in outdoor conditions receiving UV radiations as also visible light waves, temperature variations coupled up by film's exposure to moisture and rain-fall. There are modern test instruments, which are well-programmed to stimulate almost real-life situations, such as QUV-100 and others. These tests provide quantification on film-properties. Those are being done since long in past.

Further, in paints other ingredients are also present to the extent of 30-35% whereas DFP is added only to about 2% max. It looks like that no concern was ever expressed on other ingredients of paints getting affected by any of the above weathering parameters, as a result of deterioration of paint film, except perhaps the concern getting expressed on fading of a few pigments. Thus it gets assumed that only the components of DFP get migrated out of the weathered dry film on receiving rains. It has by now become a fixed notion. The stand on bad weathering leading to microbial growth on film became common, which biocide suppliers only promoted to provide the explanation on the lowered performance of DFPs. This stand is however in total contradiction to the progressive improvement being achieved on paint film properties by way of on-going continued research in paint industry year on year, as numerous scientific publications claim each year.

None thought that DFPs needed to be improved so as to arrest their leach out from the paint film, which takes place even before the weathering of the film has actually occurred.

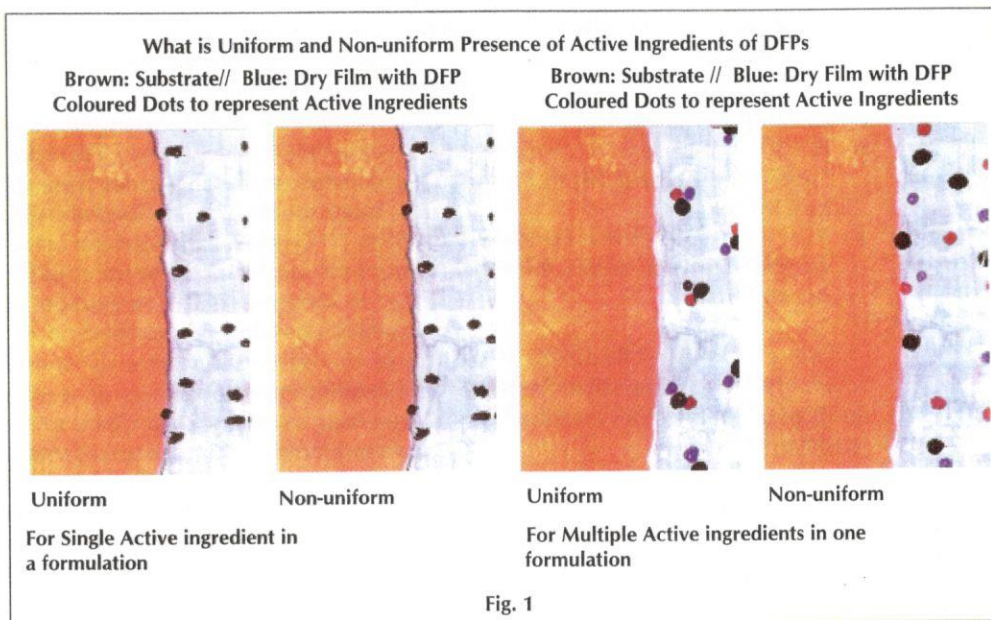
The stand on 'Weathering debacle of the film and so of DFPs' continued to be advanced from the decades in past. It provided to a layman 'a reason to believe' why the paint failed to maintain its film-integrity when microbial attack occurred on dry paint, and so why his money's worth could be only partly met with. It also provided convenience for Paint Industry to state 'Warranty Clause' on label of such paints. It helped biocide manufacturers to sell more quantum of DFP by recommending additional compensatory portion of dosage.. However, even after having conducted actual exposure study for a few years to get convinced on having received right DFP, the problems on paints in field have been continuing. But what is being achieved by doing such exposure study was not evaluated.

The real two reasons behind poor performance on which in earlier times, hardly anyone from Biocide Industry paid any attention were:

1. The most-likely non-uniform presence of the components of DFPs in dry film, and
2. The leaching of the ingredients of DFPs due to misunderstood formulation concepts of DFPs and user's demand on very stable dispersion becoming a requirement for doing such formulation

The present Author for the first time addressed on both these issues at the Biocide Conference II in Berlin in 2005 Ref 1 and from that, introduced Polyencapsulated DFPs. It offered revolutionary solution on DFPs for the paints to have longer life as dry film and which abolished a few ruling myths too. Please Refer to Figure 1 to understand what uniform distribution and presence of DFP in dry film means.

Thus, the aim should always be to ensure that DFP components remains uniformly present in Dry Film of Paints if longer life of Dry Film is to be expected, which became possible by encapsulating them together. If a DFP is offered based on single active substance, say algacide or fungicide, it is immaterial whether it is in encapsulated or embedded form or not while making its dispersion. This would become clear from the Figure 1. Against



this however, claim on uniform presence of DFP is unfortunately being made by a few on the DFPs containing single active substance said to be in encapsulated or micro-embedded form. It involves absurdum. This issue is dealt again in details later.

Further, the leaching of the active ingredients of DFPs had been found by experience, by empirical observations, but it is not desirable. However, biocide manufacturers assumed that such leaching means the active surface of dry film is getting rejuvenated, which thereby disallows microbial growth on the film. Many from Biocide Industry therefore used to convey to the user 'the leaching' as an essential functional characteristic of DFP. To support this thought, they used to show to the users "Zone of Inhibition", which gets displayed in microbial investigations done in laboratory on paint films by using plating method for such investigations. It was being shown as if such zone is forming a 'no entry area' for microbes and hence desirably existing on dry film too. DFPs were actually getting sold by showing the Zone of Inhibition seen in lab-tests around paint film. (Refer to Figure II) It is not the Zone of Inhibition, but the "Zone of Spread of DFP by Leach-out." Such leach-out and spread has to be minimal.

Thus, the Zone of Inhibition had been another myth out of mis-conception promoted in earlier years by few EU biocide manufacturers.

Such leaching is caused mostly due to wrong formulation techniques of DFP and to some extent of paints too. This was completely neglected. Since the propaganda had been done on desirability of leaching at least to some extent, DFPs were getting sold under that umbrella.

As said, the Author first time addressed this subject Ref 1 and brought to the notice that the usage of excessive surfactants in the formulation for achieving very stable dispersion created pseudo-solubility of otherwise water-insoluble active ingredients used in DFPs. As a result, almost water-insoluble active ingredients started getting washed out, being referred to as the "Leaching of the Preservatives" from a dry paint film.

Also it is worth to note that a DFP as a dispersion, which is supposed to be added in paint at the dosage of about 2% max, has to get well-covered by film-forming polymer-base of the paint as happens to other components too present to more than 30-35% in paints. For that, maintaining the appropriate PVC of the paint becomes essential. When other components of the paints do not leach out from the paint having right PVC when the film

dries and faces weathering, apparently since those component get well-covered by polymer-matrix of paint, why only DFP from such paint too undergoes leach-out? The film may crack and/or delaminate if its PVC is inappropriate, but even then its other components do not leach out. The Author proved that leaching of DFP-components gets pronounced when such components get covered first by the surfactants while attempting to achieve their stable aqueous dispersion by usage of such surfactants, and due to these surfactants, there could be existence of a partition between such surfactant-

coated actives and polymer-matrix of paint.

The work done on Polyencapsulated DFP thus became a turning point from the way Biocide Industry worked earlier, thereby abolishing quite a few older myths. Unfortunately, newer myths have now started getting established in the minds of the users. This subject therefore needs to be reviewed.

Biocide manufacturers realized the importance and impact of encapsulating

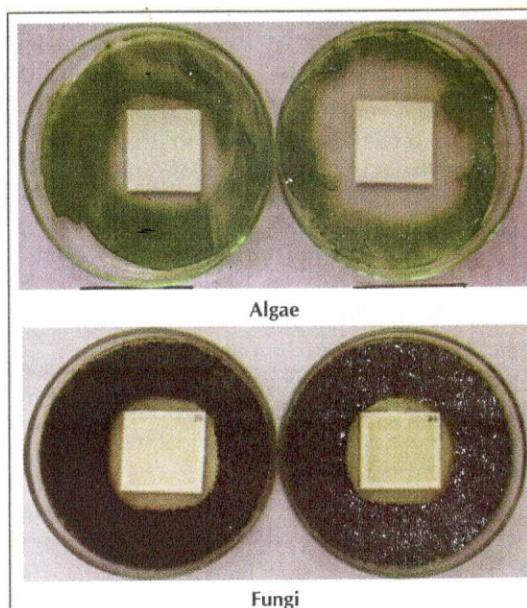


Fig. 2: The blank area around the Dry Paint Film placed in center, in the tests conducted by Plating Method, was being called as 'Zone of Inhibition for Microbes'.

three active technical ingredients of DFP together. Other biocide manufacturer/s made similar attempts and of late DFPs with corresponding claims have been brought into market. Those are said to be designed by embedding individually the technical grade active substances used in DFPs. A few performance-claims are thereafter made on such formulations. However, these claims appear to mislead the users. Those would also create newer myths.

Before going into those details, first a question arises, isn't the paint-polymer doing identical function as embedding, that is covering well all the added ingredients in it, as the word 'embedding' suggests? This has been already discussed above. So what is the extra that is being achieved from the claim of having done encapsulation or embedding of each technical active individually first, and then adding these so-embedded actives, each becoming as individual DFP product in paint, and such DFP getting covered by paint-polymer again? Would such embedded active substance really remain uniformly distributed in dry film to enhance its performance? More likely it is that each such individually embedded technical active will disperse in paint in equally random manner when paint dries. (Please refer to Fig 1 once again, to understand uniform and non-uniform presence of components of DFP.)

Therefore, it is feared that embedding each component individually before adding it to paint would serve no extra purpose; that it is a mis-conception; and therefore further claims from such material acting as an improvised DFP would be misleading the users.

Further, one has been reading the claims made on such singly encapsulated/micro-embedded DFPs. From scientific views, these have been inviting more questions on validations done before making such claims.

The major performance-claims are:

- Having achieved slow release of the technical active from micro-embedded/encapsulated formulation
- Having achieved reduced leaching

of active ingredient from such formulation

- Having achieved improved alkalinity resistance
- Having achieved reduced Environment and Mammalian toxicity
- Having achieved reduced weatherability of paints amongst few others.

The claim on "Reduction of Environment and Mammalian Toxicity" needs to be thrashed out first. It is very sensitive claim.

To be specific now, if a technical active ingredient is claimed to be showing such change of basic property, say of Diuron or Carbendazim or OIT, or anyone, by doing encapsulation/micro-embedding as a process carried out on individual substance by manufacturer/s of DFP, it would mean that a newer technical substance, which is different from Diuron or Carbendazim or OIT or any active ingredient, is getting formed by doing such modification on each. Therefore it could be argued that the resultant substance is not the same as the original technical active ingredient. At the most it would have been appropriate to make a claim that such processing resulted into an improvised status for handling the technical active, but no such statement has been made by the claimants. Therefore, it would clearly mean that there is a need for entering into newer Regulatory regime of technical evaluation and decisions on resultant substance, since newer compound seems to have been formed by such embedding as per claims made. The Regulators need to consider this seriously.

It also gets implied from the claim made that by per gram of usage of such embedded material, it selectively lowers only the toxicity but is not lowering the basic activity of the technical substance from its initial status. Such 'claimed selectivity' of only one function, only on toxicity, can be challenged and needs to be challenged. The question therefore is, has the herbicidal activity of Diuron been getting lowered or enhanced by such encapsulation or embedding practices?

Can any manufacturer claim that by encapsulation/micro-embedding, the original technical active got selectively transformed to show only the lowered toxicity? Or is he attempting to claim that there happens to be altered degree of the probable spoilage of the Environment, which is due to altered degree of leach-out of the said component from film to the environment? The reduction of leaching would mostly depend on the way the said processing of micro-embedding/encapsulation is done. But presenting a series of such claims to the user-industry in an ambiguous manner is the extension of the way in which a few from biocide industry worked in earlier decades too for creating myths on products, so as to capture the market for them.

It is therefore better to realize once again, what the purpose behind Polyencapsulation declared earlier was and what was achieved. For that, it is also essential to realize what could be the most appropriate encapsulating media and which cannot be; and how the said processing could be done. Such polymeric substances could be from the selected ionomers, dendrimers, cellulotics, synthetic polymer emulsions compatible with paint-polymer, a complex silicate polymer having molecular-voids in it, silicones and others, but which are not easily water-soluble. The most preferred medium is either ionomer or dendrimer. The Author displayed schematically the process of Polyencapsulation followed Ref 1, as also provided the proof of having achieved it.

In sharp contrast, wouldn't it be surprising to note if a biocide manufacturer declares that the encapsulation or micro-embedding of Diuron or Carbendazim or similar water insoluble technical active has been done in EO-PO co-polymer? Such polymer can be a surfactant or commercially available multifunctional linear PEG/PPG ethers, unless those are specifically designed dendrimers from EO and hence being called specifically only as dendrimer. No such claim has been made till now, which needs to be noted, and hence original claim cannot be suitably changed overnight. Can former two of EO-PO condensates be considered as

tangible polymers from the view of film-forming polymers used in paints? Linear ethers are solvents. The question would definitely arise, where would such substance remain as the paint would dry to form a film. Being non-volatile, such substance would always remain in dry film in the micro free-spaces between the lattices of the dried polymer matrix. It can easily get washed out from those areas, which would in turn introduce pin-hole porosity in the film. From such pin-holes there would be further water-ingress, and with it, the subsequent ill-effects to the film would get initiated.

Frankly speaking, when EO-PO co-polymer is said to be used for encapsulation or micro-embedding, and then a DFP is said to be manufactured, it would mean playing with 'solvation index' of the paint system without informing the paint manufacturers on most likely ill-effects from such DFPs. Most EO-PO co-polymers are known to increase the detergency of the formulation. Other few may not allow formation of hard film of paint, or would affect the hardness and other properties of paint polymer due to enhanced solvency-characteristics of EO-PO copolymer. Both mean, by using such co-polymer there would be more solubility of coated micronized Diuron or Carbendazim, which clearly means there are higher chances of their faster leaching out from dry film! However the claims made on the embedded DFP product is exactly opposite to the factual reality as presented now. The claim states 'Slow release' as a property achieved, which is thus incomprehensible. Such claim therefore would become a myth and mis-guiding factor.

The Author had mentioned earlier that Polyencapsulated preservatives in future would invite Regulators to consider more appropriately and seriously the likely existence of the concept of 'Synergy of Activity' getting built up by the contributions from each active ingredient when those are brought together as encapsulated. That means, such combination in very high probability might end up in the newer level of "Higher antimicrobial activity from such combinations" or "Modified increased toxicity", or both. It is very

serious subject. It also means, even with right kind of encapsulation carried out, there are chances that the ratio in which these actives are used together in a DFP can be significantly decreased from their today-ruling combination-ratio found empirically earlier. It is also likely that an increase in toxicity level of the formulation so-done, when the original ratio of active ingredient was not altered, can get mis-interpreted as 'Increase of Efficacy of the Product', which is a big risk. To avoid latter, there would be therefore further requirement of identifying the contents of the toxicity newly generated from the interactions of the encapsulated technical actives together. It is so, since the resultant combination may increase the formation of toxins, whereby it may not be appropriate then to call it as efficient biocide, since those may end into having strong and persistent anti-effects, and can become POP. However, it looks like that a few from biocide industry have been inclined to make the selective claim on 'Improved Efficacy' from micro-embedded DFPs, without making any reference to the status-toxicity. By presenting such selectively convenient assumptions, those are creating myths in the minds of the users. It is objectionable to make a selective claim without providing scientific Data. Obviously, long term evaluation on Toxicity profile and identification of toxic elements towards Human as also Environment, need to be systematically done. Such Data needs to reach to customers. Thereafter for its usage, the dosage of DFP on which such Data has been generated cannot be changed, and hence one cannot do free-will recommendations on altering the dosage of such DFP to the users or recommending to do further combinations of such DFP with other active ingredients. However, Charts are being displayed by such manufacturers of embedded DFPs, for making performance-claims, by showing different Fungicide and Herbicide brought together in different proportions along with such DFP, in which one of the technical ingredient is in the form of micro-embedding done. Such display silently suggests that a customer can use an embedded-product/s in any random manner with other products and in any proportion, but would still get the

suggestively selective result! Such performance-claim is definitely objectional and cannot become permissible practice from the Regulatory views too. Also, such suggestive Chart having such variables truly concludes nothing specific on performance, but leaves everything to the user to imagine, and if at all to conclude from the experiments carried out as he would like to. In most likelihood, restrictions would get slapped from the Regulators, if they happen to know on free-willed recommendations being done on the usage of the embedded DFPs. Therefore, it appears that biocide manufacturer has held with him an escape route too by leaving it to the user to try out the combinations by his own experiments, so as to avoid coming under Regulatory restrictions.. It is also feared that the unsupported claims of vague nature on such DFPs might lead to more damages later. Do we afford this?

Against the above referred essentially required dosage stipulation once for all as maximum allowable, there is another important subject to discuss on. If a biocide manufacturer states the activity-threshold of Diuron as around 540 ppm, there would be a question, why in first place 10000 ppm content of technical grade active ingredient Diuron, that too appearing in DFP in 'embedded' form, needs to be added in paints or is getting on average recommended to the user. This becomes 20 times the threshold activity number. (The question "what should be allowable level of concentration of Diuron in paints" is being asked by Indian Regulators again and again, since they happened to notice too high and randomly decided usage of such active ingredient being done in Indian Paints. Precise answer on each is not provided; but there is endless continuation of debate, which are the facts). Is it that DFP manufacturer has assumed that certain quantity of DFP has to be added in Paints, and only thereby certain performance in terms of number of years of the life of Paint-film can be guaranteed? There is no possibility of reaching to a conclusion on any such co-relationship between the dosage of DFP and number of years of performance, at least as on today till all variables are brought under frozen controls in such study. But Charts are shown by biocide

sellers specifying the recommended and essential Diuron content, that too in embedded or encapsulated form, as 2000 ppm for Standard Paint, 5000 ppm for Medium Quality Paints and then with a big jump to 20000 ppm of technical active (which means 40 times of the threshold requirement) for Premium quality paints (stating 5-7 of years of film life of such paints).

If Premium Quality Paint is said to be getting formulated with the best of technology incorporated, with the most ideal PVC, with premium quality of binder used as also pigments and titanium dioxide, thus having far better film properties including weathering-resistance, the question definitely arises: why in it higher dosage of DFP with respect to active content of Diuron (that means 20000 ppm of Diuron) is being recommended or is said to be essential? It should be opposite: one needed to say that premium grade paints would require lesser dose of DFP, and so it becomes worth to make better grade of paints and reduce the risk of using higher content of Diuron!! In other words, with the reasonably sufficient dosage of right type of DFP, but which would be lower than the one used in other paints, premium paint must give 5-7 years of life. For that to happen, the formulation of DFP has to be almost perfect, to ensure that from such paint-film, the active contents of DFP would not easily migrate out by leaching. In sharp contrast, DFP manufacturers making claims of having done embedding of the technical actives seem to be aware that the said DFP would leach out badly, which apparently has been making them to recommend high ppm usage of DFP with respect to the total content of technical active/s. This needs to be noted.

Therefore, all the talk that reaches to

Paint Industry on the guarantee to be given on number of years of film-life, supposedly based on higher dosage of DFP as essentially required, seems to be actually showing to the paint manufacturers only one equation: That is: "Paint Manufacturer's affordability quotient on excessive-usage of DFP in paints vs Competitive Marketing Advantage that he is likely to gain thereafter by using the word Guarantee". Thus it looks to be assumed that a paint manufacturer has to solve that equation as per raw material inputs commercially available to him to meet the claim on guarantee. Therefore it also seems that biocide manufacturers have continued to pass on all the responsibilities to Paint Industry to decide what they would like to do, as becoming the strategic commercial policy to sell such DFPs.

However, it is certain that 'one has to accept that there seems to be unwanted excessive usage of biocides and DFPs, that such excessive consumption is not advisable and hence has to be reduced'. Only an ethical manufacturer of biocides would take such responsibility.

If anyone still insists that there is above kind of dosage-relationship to life of the paint film, it is feared that it will remain as an ever-lasting myth, till inevitably the regulatory steps take control and rule over on such myth.

There is another point worth noting. By way of encapsulation/ micro-embedding by using EO-PO co-polymer to do so, when a claim on having achieved Reduced Mammalian Toxicity is made, it needs to be considered on priority. In first place, Diuron does not have significant Mammalian toxicity profile, Carbendazim though is being considered as mutagen. The claim seems to be in circulation, on having

achieved reduced skin-irritation by whatever method of such study followed. The reduction of skin-irritation from the embedded formulation of Diuron or Carbendazim or OIT may be on account of quick washability of the skin free of Diuron or OIT like molecules, which is no doubt due to high detergency of the EO-PO co-polymer used, enabling their complete and quicker washability from skin, and thereby on account of their reduced absorption in skin. Thus higher level of detergency is the main contributory factor towards this claim is obvious. But by the same scientific logic, it also means there is quick washability of such ingredients from the dry film too due to increased detergency caused by EO-PO copolymer, on which enough has been talked earlier. It is therefore surprising to note that two contrasting claims get made on one and the same product. Such contradiction is bound to confuse an alert user, who would raise many questions thereafter.

In conclusion, in the absence of detailed declaration by studies conducted with validation, one cannot afford to go by the presented newer myths, which seem to be originating from commercial considerations given only to competitive-business-potency. It would mean on scientific front coming back to square one position on DFPs within short time, and once again back on the same issues related to Environment Conservations, etc.

References

1. Polyencapsulated DFP, A Better Alternative, Dr. P. Pathare, Novel Biocide II Conference, European Coatings, Berlin, Feb. 24/25, 2005.
2. Dendrimers: Synthesis, Applications, and Properties, Elham Abbasi, et al, Nanoscale Res Letters, 9, (1) 247, 2014, abstracted and e-copy Springer. ■

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