

## **BLEEDING OF OIL-TYPE / OILBORNE WOOD PRESERVATIVES**

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### **ABSTRACT**

Bleeding of all oil-borne/oil type wood preservatives has been any issue since the early 1800's. The general conclusions are that most bleeding is due to entrapped oil in the wood cells, and upon expansion or relaxation, the oil trapped inside the wood forces the oily preservatives to the surface. Historically, copper naphthenate has shown less bleeding than either creosote or pentachlorophenol solutions or treated wood; this phenomena may be due to it being a lesser used product over the last 4 decades and that the treaters using this product have usually be those treaters classified as the most caring about appearance. Slumping, or the movement of oil borne preservatives due to gravity, from an upper position, as in poles, to the groundline is beneficial and not considered a detriment to the treatment, but an advantage, as long as the oil around the pole base is not excessive. Many processes can be employed to minimize bleeding, and included in those processes are items such as extended final vacuum, longer expansion baths, efforts to slow thru-plant processing of poles, and final steaming. Generally all bleeding can be controlled by the wood treater and is generally not thought to be a characteristic of the treating solution itself.

## **INTRODUCTION**

### **Oil-borne wood preservatives**

Oil borne wood preservatives fall into two main groups: The first group includes creosote, creosote-coal tar, and creosote-petroleum formulations. The second group consists of solutions of chemicals dissolved in a non aqueous carrier. This include penta, copper naphthenate, oxine copper, bis(tri-n-butyltin)oxide, 3-iodo-2-propynyl butyl carbamate (IPBC), chlorothalonil, the triazoles, chlorpyrifos, and chlorothalonil/chlorpyrifos among others. Creosote is not always dissolved in oil, but it has properties that make it look and feel oily (Lebow and Tippie 2001). Petroleum-base carriers are commonly used in oil-borne preservative formulations. These preservatives form a resistant envelope on the wood surface, act as water repellants, allow treatment of wood after machining, reduce splitting and checking and there is no renewed wetting after treatment.

After wood is treated with an oil-type preservative, varying percentages of the preservative may come to the surface, if the volatility or distillation range of the oil is such that a residue remains on the surface the term 'bleeding' is generally applied. This is observed predominantly in creosote and penta treated wood. If the preservative is a crystal-type dissolved in a petroleum carrier of high volatility that none of it remains on the surface of the wood after exudation, and only the preservative crystals are deposited, the term 'blooming' is applied. Penta undergoes blooming in some solvents, like naphtha or mineral spirits since it lowers the surface tension of the solvent. Many users of poles and railroad ties are more interested in long life than in cleanliness of the surface and do not invest in obtaining cleaner surfaces (Mayfield 1954).

### **Creosote and Pentachlorophenol**

Creosote a distillate produced by high temperature carbonization of bituminous coal, has a long record of satisfactory performance as a wood preservative. It is used for railway ties (often blended with heavy petroleum oil), utility poles, marine piling and timbers for highway construction where surface appearance of the treated wood is of minor importance. The black color, the strong odor, and the difficulty in finishing make it

unsuitable for many applications. Creosote is a variable mixture of different classes of more than 300 organic compounds, the most predominant being the polycyclic aromatic hydrocarbons (PAHs). PAHs can constitute up to 90% of creosote with 20-40% of the total weight attributed to just sixteen PAHs. Other components are phenolics (1-3%), nitrogen-containing heterocyclics (1-3%), sulphur-containing heterocyclics (1-3 % of creosote), oxygen-containing heterocyclics including dibenzofurans (5-7.5 % of creosote). Different studies reveal varying proportions (Chakraborty 2001; Melber et al 2004). A full analysis of a particular creosote is not possible. The chemical composition and properties of creosotes are influenced by the origin of the coal and also by the nature of the distilling process. The volatilization, leachability or bleeding extend of creosote is variable because of the number of compounds involved and is difficult to characterize (Melber et al 2004).

According AWWA P8 Penta solutions for wood preservation shall contain not less than 95% chlorinated phenols. Penta was one of the most widely used biocides in the U.S. before regulatory actions cancelled and restricted certain non wood-preserved uses in 1987. All penta produced in the United-States is now used in pressure-treatment of wood for railroad ties, pilings, posts, cross arms, and utility poles. Penta is highly effective and was historically rated the least expensive of the three major preservatives at least before the rising cost of petroleum in 1979. It is dissolved in petroleum or other organic solvents that allows it to adequately penetrate wood. The efficacy results of pole service and field tests on wood treated with 5% penta in heavy petroleum oil are similar to those with coal-tar creosote. This similarity has been recognized in the retention requirements of treatment specifications (Freeman, 2005 & Johnson and Thornton 2000; Scheffer et al., 1997).

## **LOSS MECHANISMS OF OIL BORNE PRESERVATIVES**

Oily materials in wood move both as a liquid and as a vapor, depending upon volatility, viscosity and other factors. Oil borne preservatives may be lost from wood in service by three mechanisms: (i) vaporization, (ii) bleeding and (iii) leaching. These processes affect the various constituents to different degrees, depending on their physicochemical properties (and possible mutual interactions). Some components are slightly water soluble, and may leach to the surroundings (Chakraborty 2001). Fractions with relatively high

vapor pressure evaporate relatively rapidly. A low boiling material will move out faster by vaporization than a higher boiling one. A higher boiling material will tend to flow out or be forced out to the surface of the wood and residual material remains on the surface after the lighter fractions have evaporated (Mayfield 1954). When out in the open, wood is exposed to UV radiation, heat (i.e., infrared radiation), rain and freezing temperatures. These result in all three mechanisms causing loss of preservative from wood surface (Chakraborty 2001).

Using sections of two new railway ties (uninstalled ties treated in 1995) and two old ties decommissioned from Toronto Transit Commission rail line after 26 years in service, Chakraborty (2001) quantified the relative amounts of creosote components lost by each of these three mechanisms under simulated field conditions. Samples were subjected to various environmental conditions by exposure to ultraviolet and infrared radiations, water spray and different temperatures. He correlated these mechanisms with vapor pressure, solubility and initial retention. His results showed that Leaching was the predominant loss mechanism for all the ties for both PAHS and phenolics. The percentage of total loss attributed to leaching ranged between 50-96%. Vaporization was prominent only in the first new tie and was surprisingly low for the second new tie possibly due to loss of the compounds from the surface during storage; the new ties were stored outside for three years before the experiments. For both bleeding and leaching, the comparative amounts lost from the four ties were observed to be proportional to the initial retentions of both PAHs and phenolics in the tie. Only leaching was an important mechanism in both new and old ties. While the percent loss was greater for the first old tie, the amounts of residual chemical content in the second old tie exceeded the former. This was because chemicals in the first old tie were retained mostly near the surface, whereas a cross-section of the second one (made of oak) revealed that penetration was non-uniform, but went to the very core of the tie leading to lower losses. Losses are very much related to the amounts of chemicals present on or near the surface. Despite the several simulated environmental exposures, the maximum amount of the initial amounts of chemicals lost from the tie surfaces did not exceed 4% for any of the compounds. In fact, for most cases, the amounts of the chemicals lost were below 1%, the maximum (3.78%) being lost from a

compound (pyrene) from a new tie. This review focuses on bleeding a characteristic of creosote and to a lesser extend Penta impregnated wood products (Chakraborty 2001).

## **BLEEDING**

Bleeding may be apparent immediately after treatment, or not become obvious until after the product is placed in service (Lebow and Tippie 2001). Bleeding is objectionable to many users of poles but some pole users and users of railroad ties in favor bleeding with the belief that the resultant coating adds to the service life of the treated wood by holding the preservative in the wood and by the prevention of checking and top shattering (Mayfield 1954).

The AWPA defines 'bleeding' as the exudation and accumulation of liquid preservative on the surface of treated wood. The exudates may evaporate, remain liquid or harden into a semi-solid state on the surface of the treated wood (Blanchard 1919). At any time after pressure impregnation with creosote, timbers may exude creosote components, either slightly or appreciably, locally or generally, temporarily or continuously. The amount that bleeds passes through a maximum, although it may subsequently fluctuate. Bleeding is a major problem mainly in creosote and to a smaller extend penta treated wood. Bleeding continues for many years and is enhanced on hot and sunny days (Blanchard 1919). Creosote bleeding can cause handling problems and has increased public concern about effects on the environment and represents economic loss (Crawford and others 2000). Rising concerns about bleeding of preservatives from highway bridges, and the potential effects on the environment, have resulted in preservative bans by some state environmental protection agencies (Wacker et al. 2003).

### **Differences in Bleeding characteristics of Creosote and Penta**

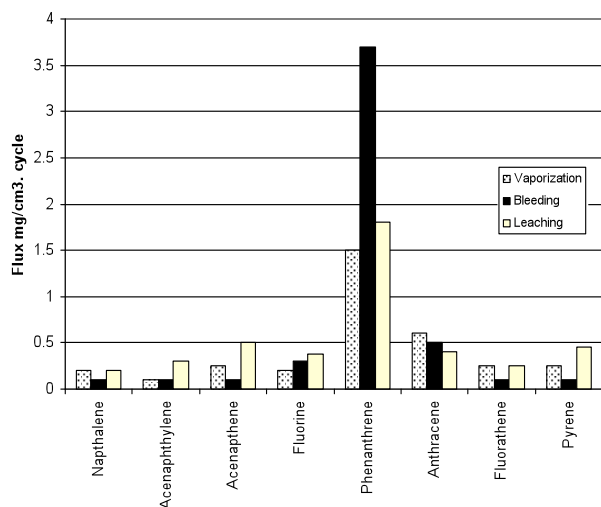
When vertically installed in field conditions creosoted poles tend to bleed on the side of the pole exposed to the heat of the sun, whereas penta treated poles tend to bleed from the entire pole surface. Secondly, when lying on skids creosoted poles normally remain dry except for a few that begin to bleed in the presence of sunlight. Because of their high surface tensions and semi solid characteristics the creosotes remain in wood at ambient

temperatures. Penta treated poles lying on skids after a period of time may have bleeding take place on the undersides of the poles as a result of more fluid petroleum and penta components moving downward by gravity (Leutritz 1957). These differences in the two preservatives may be attributed to their distillation products. Creosote is a highly complex material with a series of aromatic hydrocarbons most of which are solids at room temperature. Creosote bleed will contain the various components which have a high boiling point and do not easily evaporate on the surface.

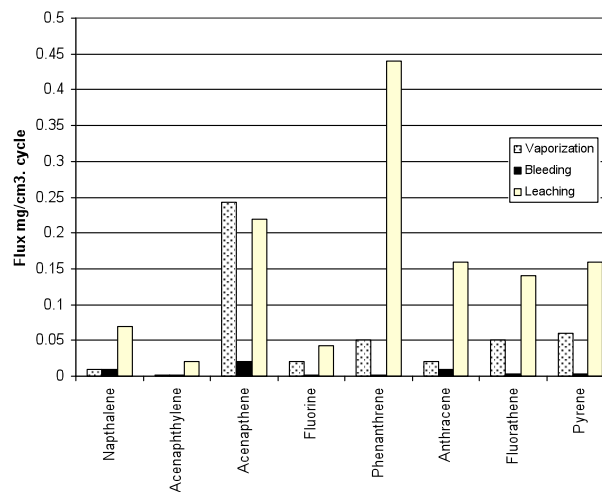
Penta and the petroleum carrier are mainly liquids at room temperature. The bleeding components will contain the phenolic components and high boiling components the petroleum carrier. Other differences may arise from method of treatment, temperature, humidity conditions and properties of the wood (Leutritz 1957).

The study mentioned above by Chakraborty (2001) quantified the relative amounts of creosote components lost by bleeding, leaching and vaporization under simulated field conditions in sections of two new railway ties (uninstalled ties treated in 1995) and two old ties decommissioned from service after 26 years. Since PAHs constitute the major portion of the creosote, analyses were restricted to eight PAH compounds only, namely: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, acenaphthene, fluoranthene and pyrene. Phenolic compounds were analyzed as total phenolics instead individual phenolic compounds. These have different aromatic ring numbers and widely varying structures and physical-chemical properties. Compounds bleeding out of the ties were absorbed by paper towels wrapped around during IR radiation. After each twenty-four-hour exposure cycle, the paper towels were unwrapped and those portions where dark-colored creosote was absorbed were cut off and creosote components were Soxhlet extracted with dichloromethane. The losses from the first new tie far exceeded losses from the other ties. High bleeding of fluoranthene, anthracene, and phenanthrene from the first new tie were consistent with the high retention of these compounds in that tie. Bleeding was negligible in the second new tie possibly because of difference in properties (such as porosity) between the two ties (Figure 1). Differences in moisture content affected the ease with which chemicals from the interior were mobilized to become more available at the

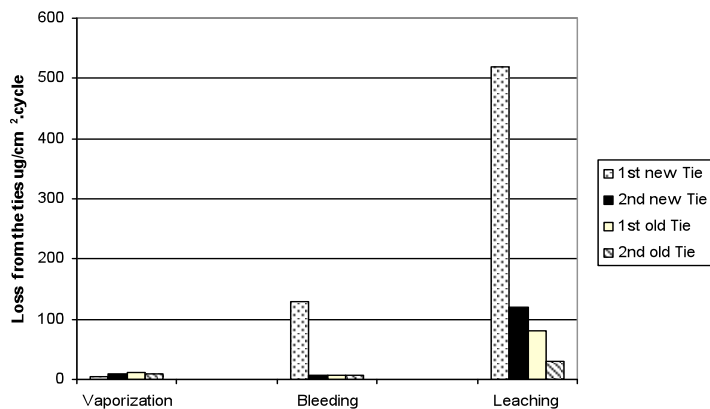
surface. There was a linear relationship between the amounts of the chemicals bled vs. the corresponding retention in the tie section. The compounds in the first new tie fit to a linear trend (regression coefficient =0.988), whereas the corresponding regression coefficient for the second new tie was 0.868. This was not observed for the old ties. The first old tie showed some bleeding only for acenaphthene, anthracene and fluoranthrene, but no linear trend. In the second old tie, the only compounds that bled were acenaphthene, fluoranthene and pyrene. Since the old ties were both in service for twenty-six years, the amount bled was small, so low levels of the compounds hampered proper detection. The average fluxes per cycle from bleeding, vaporization and leaching are plotted below. The amounts of the total phenolics lost by the different processes after five cycles are shown in Figure 2. Bleeding of phenolics was only significant in the first new tie.



**Fig 1a. Comparative loss from the 1<sup>st</sup> new Tie.**  
**Comparative loss from the 1<sup>st</sup> old Tie.**



**Fig 1b.**



**Fig 2. Comparison of losses of phenolic compounds by different mechanisms from the four ties**

### **TRAPPED AIR AND EXCESSIVE SURFACE RETENTION -THE CAUSES OF BLEEDING**

The most important driving force behind the greater bleeding tendency of seasoned wood is the presence of air trapped in the wood after treatment (Thompson 1974; Kelso and Parikh 1976).

As early as 1919, a study recorded by Blanchard et al. indicated that bleeding is caused to a large extent by the expansion of air in the wood cells. Trapped air in the cells has pressure higher than atmospheric at the completion of an empty-cell treatment cycle. Trapped air is relied on to eject excess preservative from wood, but this expulsion continues particularly with creosote and petroleum components of relatively high viscosity after the wood is removed from the chamber. Exit of entrapped air accounts for the initial stages of bleeding. In many yards creosote poles are stored 6-12 months to permit creosote to drip free. Movement of air in and out of the timber exacerbates exudation. On a cool night, air in the timber contracts and draws in additional air. During the heat of the day the air expands and tends to force out some of the preservative near the surface. As wood is heated it also expands and this pressure forces some oil to the surface

The second major contributing cause of bleeding is excessive absorption of preservative by some timbers resulting in excessive high concentration or retention of preservative near the surface of the treated piece (Mayfield 1954; Richardson 1993). Even in the case of thick sapwood southern pine poles treated to an 8 lb. retention, there may be 16 lbs/ft<sup>3</sup> of preservative in the outer one-eighth inch. The preservative is brought to the surface by many different forces. For example natural gravity flow in a vertical piece drives the preservative down and outwards (Mayfield 1954; Hartfield and Allen 1961). The excess retention can occur because of the expansion of the liquid within the cell due to increased temperatures, by the accumulation of water in the cells and its expansion, causing the liquid preservative to be ejected from the cells. Under any given set of conditions wood has an equilibrium or critical non bleeding retention of preservative. When this is exceeded, preservative moves out to the surface (Leutritz 1957; Hartfield and Allen 1961).

Additional variables frequently mentioned as contributing to bleeding include intensity of initial air pressure, volatility of the solvent and the external pressure exerted up on the wood (Kelso and Parikh 1976). All vacuum and pressure impregnation processes are basically similar and involve loading, vacuum or pressure, flooding the cylinder with preservative, draining the cylinder and adjusting the pressure of air within wood and finally returning the wood to atmospheric pressure. The degree of recovery depends upon the relationship between the initial and final air pressures and the tendency to bleed depends on how these pressures relate to atmospheric pressures. Bleeding once established will continue until the internal pressure comes to equilibrium with that in the surrounding atmosphere, or a sufficient quantity of the petroleum carrier on the wood surface is evaporated so that the remaining residue is dry or a sufficient quantity of the free preservative solution in the cells near the surface is removed by either active bleeding or evaporation (Kelso and Parikh 1976). The entrance of moisture in wood causes some expansion and since water tends to displace oil in wood, variations in moisture content might cause some exudation. Water in wood expands on freezing and might force oil to the surface.

All of the above factors are greater on the side of the piece where the temperature is higher and the oil less viscous due to heat of the sun. If the process of treatment could be conducted so that there would not be a high concentration of preservative near the surface, exudation would be greatly reduced (Mayfield 1954). When wood samples are evacuated of air and then treated to saturation with petroleum, it results in very high retentions and no bleeding because of absence of air. Subsequent air pressure on these samples results in bleeding. A test showed that when these samples were treated with water, the water displaces some of the surface oil resulting in a lower retention of oil at the surface and less likelihood of bleeding (Leutritz 1957).

### **BLEEDING IN GLULAM TIMBER BRIDGE COMPONENTS**

Most bridge components are constructed using a combination of glued-laminated (glulam) and solid timber. Excessive bleeding in bridge components may be attributed to use of glulam components and compressive stress. In the summer of 2000, Wacker et al. (2003) visually inspected six creosote-treated (empty cell process) timber bridge superstructures in Michigan's lower peninsula and removed sample cores to find reasons for reported excessive creosote bleeding. Surfaces with exposure to direct sunlight were covered with a thick layer of crude. The age of the bridges varied from 1-10 years. Five of the six bridges were constructed with glulam timber components. Visual inspections focused on the condition of the treated wood and photographic documentation of the preservative surface residues or evidence of bleeding. In general, most glulam members had significantly higher creosote retention than the minimum required by AWWA (C28). Residual creosote retention levels ranged between 5.1-52.2 lb/ft<sup>3</sup> with glulam members having significantly higher amounts than sawn lumber. Glulam members are more susceptible to high preservative retention levels during pressure treatment because of the low moisture content required during the adhesive bonding fabrication process and the higher percentage of sapwood compared with that in sawn lumber. The high compressive stress continually applied to the deck laminations in a stress-laminated bridge (five of the six bridges are stress-laminated) may have contributed to magnifying the creosote bleeding problems. More bleeding was noticeable at the lamination interfaces and may indicate a compression-related problem (Wacker et al. 2003).

## **FACTORS AFFECTING BLEEDING IN CREOSOTE AND PENTA TREATED TIMBER**

From the several studies performed since the early 20<sup>th</sup> century, many investigators have studied the phenomenon of bleeding. Their answers have been varied and often times contradictory (Kelso and Parikh 1976). The following paragraphs summarize a number of factors that are reported to influence the occurrence and extend of bleeding.

***Retention, distribution and absorption of preservative and/or solvent:*** Effect of retention has already been discussed in sections above. Operating companies report bleeding on poles with higher retentions. In most cases, a linear relation is observed between the amount bled and the initial content of the chemicals in the ties and poles, particularly for the newly treated ones (Mayfield 1954; Hatfield and Allen 1961; Chakraborty 2001). The fibers of wood act as bundles of capillary tubes. When pressure is used, the tendency for the pole to bleed and the rapidity of bleeding depend on amount of excess oil over normal capillary absorption, so that poles with large excesses of oil will bleed extensively (Leutritz 1957; Mayfield 1954).

***Penetration and Distribution of preservative in wood:*** The usual treating processes give a heavy concentration of preservative near the outside which tends to move to the surface. Treatment and conditioning methods should aim at moving the point of highest concentration to a position just far enough inside the wood to prevent exudation. Inadequate penetration of preservative results in more exudation in material (Mayfield 1954). Bleeding may be most severe on the southern half of poles because of preservative migration due to gravity especially in penta poles (Hatfield and Allen 1991).

***Physical Properties of the preservatives and Solvent carrier:*** The higher the surface tension of the liquid, the more liquid the wood can hold. Poles treated with high surface tension preservatives will permit higher retention and have fewer tendencies to bleed. Low viscosity preservatives tend to bleed more rapidly. There is a close relationship between viscosity and capillary action although the effect of viscosity may be masked by evaporation or distillation pattern. Taken alone, viscosity may or may not be a factor in

bleeding. The amount and type of residue may be the important factors rather than the viscosity (Mayfield 1954). High boiling residual, either from coal tar (pitch) or petroleum tends to cause bleeding when in preservative. Operating companies report bleeding on poles treated with creosotes having heavier proportions of higher boiling point constituents-highest residues distilling above 355°C. Viscosity is a function of the residue (Hatfield and Allen 1961). If the preservative is entirely a distillate, the tendency toward bleeding is not nearly so marked. The greater the amount of high boiling material, the more tendency toward bleeding or the more tendency for the material which exudes to remain on the surface after the lighter fractions have evaporated (Mayfield 1954). Preservatives with higher proportions of the lighter constituents lose these more volatile proportions by evaporation. The rapidity with which the non-bleeding retention is reached is affected by evaporation. The faster some components are lost by evaporation, the quicker the critical retention for bleeding will be reached. There is a direct correlation between the distillation pattern and the rapidity with which a critical non-bleeding retention is reached by evaporation. Low surface tension preservatives are retained less easily by wood, and if the critical retention is reached and the preservative solution or carrier does not evaporate rapidly as it comes to the surface, bleeding will take place (Leutritz 1957).

Properties of the solvent used will influence the extent of bleeding especially for Penta. The performance of and the properties of the treated wood are influenced also by the the solvent (Ibach 1999). The AWWA P9 standard defines solvents and formulations for organic preservatives. Penta can be dissolved in oils having a wide range of viscosity and vapor pressure. AWWA P9 Hydrocarbon solvent type A composed of petroleum distillates or a blend of petroleum distillates and co solvents is preferable for maximum protection, particularly when the wood is used in ground contact and bridge applications. Heavy oils remain in the wood for a long time but are prone to bleeding. AWWA P9 Type C solvent (light Petroleum solvent light oil) is used when treating glulam. Type E solvent (dispersion in water), is only approved for aboveground use in lumber, bridge ties, mine ties, and plywood for southern pines, coastal Douglas-fir, and redwood (Ibach 1999). Petroleums have at usual atmospheric pressure a lower surface tension and a lower viscosity than creosote. Because of lower surface tension, less petroleum is retained by wood and

because of lower viscosity, the oil should bleed faster if critical retention is exceeded. However, if a wood is treated with very light petroleum, evaporation is so rapid that the liquid in the outer fibers of the wood never exceeds the critical retention and bleeding never takes place. Because of the high proportions of liquid constituents in petroleum, the petroleum base of Penta be lost faster through evaporation rather than bleeding (Leutritz 1957).

***Species and Properties of the wood:*** Wood properties influencing bleeding include: specific gravity, irregularities of the capillaries and amount moisture in the wood cells. Light weight wood will take up more preservatives than woods with higher specific gravities. However, critical non bleeding retention is about the same regardless of specific gravity. Initial retentions have been found to vary with specific gravity, but after bleeding, the average equilibrium or critical non-bleeding retention is a constant approx. 7.5lb/ft<sup>3</sup> of wood (Leutritz 1957). Refractive species that are difficult to treat and resinous woods exude more. This is most likely attributed to presence of preservative on the surface due to lack of adequate penetration.

***Climate and Weather conditions in service or storage:*** Bleeding is stimulated by sunlight, probably due to the timber becoming heated by absorption of solar radiation resulting in some expansion and contraction in wood (Mayfield 1954; Hatfield and Allen 1961; Chakraborty 2001). The heating also lowers the viscosity of the oil and causing it to flow out. In addition temperature increase expands internal air and water forcing oil preservatives to the surface (Leutritz 1957). The wood not only becomes hotter, but also acts as a collector for particulate substances floating around in the atmosphere causing the surface to appear darker and hotter. Moisture uptake has a major effect on bleeding. After heavy rains, creosoted poles are likely to bleed more. Poles which warm during the day, absorb humid air or water as they cool at night. On the following day the sun heats the surfaces and increases tendency to bleed (Mayfield 1954). The heat melts the tarry semi solid constituents of creosote in the outer layers of wood (Leutritz 1957). Generally poles exude less in cold weather, except in cases when exudation may result from freezing of water in the poles (Mayfield 1954).

***Amount of insolubles and water emulsion in preservative:***When true insolubles (dirt, carbon, etc) are high they may deposit in appreciable depth on the surface of wood, tending to induce bleeding. AWWPA specifications are on the safe side in preventing this cause of bleeding. Emulsion in preservative tends to filter out on the surface of wood, leaving a deposit. Water content should be held not over 2% in preservative. Accumulation of blown material; dust, sand, cinders, etc. on treated wood retards the evaporation of the excess preservative or solvent which flows to the surface hence increasing bleeding (Mayfield 1954).

***Treatment and Seasoning method:*** Test posts treated by 12-lb. and 8-lb. full-cell processes bleed more than similar specimens treated by 8-lb. empty-cell processes (Hatfield 1961). In the empty cell treatment method, poles are steam conditioned followed by initial vacuum period. Air pressure is then applied as the preservative is forced in. When the pressure is removed the preservative kicks back or partially bubbles out of the wood. Unless care is exercised, the empty cell method may permit more preservative to be brought to the outer fibers and thus increase likelihood of bleeding. It however results in better penetration (Leutritz 1957). Insufficient vacuum after steaming leaves excess water near the surface which tends to cause exudation. Timber which has been floated or ponded (water stored) or conditioned by immersing in water or seasoned slowly from a high initial moisture content is more permeable to creosote and therefore, less likely to bleed (Chakraborty 2001). Final steaming or use of an expansion bath raises the surface temperature of the wood, lowers viscosity of the preservative, expands the air in the wood so that more oil is blown out and, causes more suction of air back into the pole after coming in contact with atmospheric conditions; all of which has a tendency to reduce exudation. Higher and longer final vacuum periods aid in the production of cleaner material (Mayfield 1954). Green timber exudes less than seasoned timber due to less surface retention. When green and dry pieces are treated together in a charge the dry pieces retain more preservative. Initial steam tends to equalize the moisture content. Charges should have uniformly seasoned material (Mayfield 1954).

***Length of time the timber is in service:*** Wood that has been longer in service has less retention at the surface hence less bleeding. After equivalent number of cycles, the total loss of compounds from two new railroad ties was found to be at least double the loss of the corresponding compounds from the two old ties. removed from the railway tracks after twenty-six years of service before being tested by Chakraborty (2001).

***Amount of sapwood-*** Sapwood is also a factor largely because of the excessive absorption of oil that it takes (higher retentions). Generally thin sapwood pieces exude more due to low penetrations in the inner timber and excessive retention in the thin sapwood (Mayfield 1954).

***Growth rate and amount of Juvenile wood:***The use of rapid growth woods increases bleeding (Richardson 1993). To satisfy the increased demand for forest products, much of the current and future timber supply will come from short-rotation plantation stock. This resource tends to contain more sapwood and higher proportions of juvenile wood resulting in excessive absorption of preservative during treatment.

## **STRATEGIES TO REDUCE BLEEDING**

The tendency of oil-type preservatives to bleed or exude from pressure-treated wood has been recognized as an undesirable property of such wood for many decades (Kelso and Parikh 1976). Bleeding can only be completely avoided if the cycle is designed to ensure that any trapped air has a pressure below atmospheric at the end of the process so that any movement of preservative will be inward rather than outwards (Richardson 1993). This may not be practically possible however wood preserving plants can do a great deal to conduct their operations in such a manner that exudation of oil-type preservatives will be minimized. From several studies the following may be incorporated to reduce the problem.

***Wood preparation:*** Presence of mold and stain may affect uniformity of treatment, greatly affect penetration and retention and consequently the occurrence of exudation. Wood should be pressure treated before molding occurs and conditioned in such manner that molding organisms are controlled (Mayfield 1954). It is important to machine-trim round

pieces. Areas on trimmed poles not reached by knives exude more. The improved surface condition effected by machine trimming may be due to removal of resin formed on the surface when the bark is removed, difference in cell content in the exposed outer layer, or opened cells on the trimmed surfaces. It is also beneficial to select material for treatment having the same degree of seasoning or condition the material in such a manner that the moisture content and distribution are as nearly uniform as possible to ensure uniform penetration and retention (Mayfield 1994). Creosote does not penetrate parts of wood with moisture above fiber saturation point hence adequate seasoning is mandatory (Bergman 1991). Bleeding can be reduced if only slow grown wood is used for poles and posts. This may not be practically possible because the current material available is all from short rotation plantations. Finally, refractory species or those with thin sapwoods should not be shipped to areas where bleeding is a particular problem as a result of weather conditions which accelerate bleeding.

***Preservative choice and cleanliness:*** Cleanliness of the preservative and treatment equipment and prevention of admixture with other preservatives will reduce bleeding incidence. Creosote may be improved by reducing the water content to about 0.5% and avoid preservative with too high distillation residue (high boiling points). For extra cleanliness, the residue of creosote used should not exceed 30%. Use an anti-blooming agent may be necessary where crystalline preservatives are dissolved in petroleum or other carrier or use a carrier with a high enough distillation range to prevent blooming (Mayfield 1954).

***Choice of solvent:*** To minimize bleeding, creosotes or petroleums of high surface tension should be used and the components that are liquid at normal temperature should be held to a practical minimum. Penta itself affects the surface tension of the petroleum in which it is dissolved. Any solute that lowers the surface tension of the solvent will tend to concentrate in the surface layer, rather than distribute throughout the fluid. This could account for the blooming or crystallization of penta on treated wood when light petroleum solvent is used. Using petroleums that have both a low boiling point portion and a high boiling point portion in which penta is very soluble may be beneficial. With a relatively large

percentage of fluids that evaporate easily from the pole, surface tension of the preservative would increase and the pole could hold more liquid without bleeding. At the same time, the high boiling point portion in the interior of the pole would have less tendency to travel to the surface and bleed because the amount of liquid the wood can hold is not exceeded (Leutritz 1957). The use of a completely volatile or recoverable solvent as a carrier for penta yields poles having a clean surface which appears untreated.

The treater should ensure any solvent used meets the P9-A standard, for boiling point range, flash point, viscosity, and water & sediment content. However the chemical composition of hydrocarbons boiling in the “diesel range” and other petroleum fractions has changed significantly since AWPA “P9 Type A” oils were first adopted in the late 1940s. U.S. federal legislation to reduce vehicular emissions was initiated with the adoption of the Clean Air Act. Diesel fuel has faced tighter specifications for aromatic content to reduce particulate matter from combustion and sulfur content to reduce sulfate and sulfuric acid pollutant emissions. The changes have not been considered in AWPA P9-A and may affect efficacy and penetration of preservative in timber in unforeseen ways.

***Choice of Straight creosote vs creosote-petroleum and creosote -coal tar Solutions:***

While creosote is not always dissolved in oil, either coal tar or petroleum oil is mixed with creosote, in various proportions to lower preservative costs. In North America, the creosote fraction is combined with correction oil or the unprocessed naphthalene to make AWPA-standard creosotes. Posts and ties treated with formulations of these solutions show better service than those similarly treated with straight creosote (Ibach 1999). Compared with straight creosote, creosote solutions reduce loadings substantially while still retaining adequate preservative properties. These solutions have a greater tendency to accumulate on the surface of the wood and bleed. They penetrate the wood with greater difficulty because they are generally more viscous than is straight creosote. High temperatures and pressures during treatment improve penetration (Ibach 1999). Today, more is added to the blend than necessary to maintain the clean-treating, easy-handling characteristics. Increasing the percentage of creosote fraction in the blend yields greater volumes of wood preservatives meeting AWPA requirements, but the resulting products are be heavier and

contain higher concentrations of PAC (phenanthrene, anthracene, carbazole). A decline in the handling characteristics and the surface cleanliness may result of the wood but the efficacy is unaffected. The AWWA P3 stipulates that creosote–petroleum oil solution shall consist solely of specified proportions of 50% coal-tar creosote by volume (which meets AWWA P1/P13) and 50% petroleum oil by volume (which meets AWWA P4). However, because no analytical standards exist to verify the compliance of P3 solutions after they have been mixed, the consumer assumes the risk of using these solutions.

***Seasoning method employed:*** Several authors have reported that unseasoned southern pine poles treated with either penta in hydrocarbon solvent or creosote following steam conditioning will be less likely to bleed than similarly treated seasoned poles. This fact has been used to produce non-bleeding southern pine poles of a uniformly light color following treatment with Penta. Unseasoned poles treated following steam conditioning are less likely to bleed because less air is trapped in the wood following treatment to cause redistribution of the preservative toward the surface as it escapes upon exposure (Hatfield and Allen 1961; Kelso and Parikh 1976). Various theories have been put forward to explain the inward movement of oil-borne preservatives upon exposure of southern pine poles treated green following steam conditioning. Creosote moves from the outer zone into the deeper zones as water is lost from the latter. Walters and Arsenault (1971) suggested that the inward movement of penta might be caused either by the solvents having enough miscibility with moisture to bring about diffusion or the moisture may have precipitated the penta in place, thereby controlling migration as a result of gravity or hydrostatic pressure. Thompson (1974) in explaining this lack of bleeding stated that because green poles have higher moisture content, little or no air is trapped in its interior following an empty cell treatment. They also conduct heat better, the interior area has a higher temperature when removed from the cylinder than a similar area in seasoned poles. As the interior area cools and contraction starts, a partial vacuum is created which reverses, reduces or completely stops outward movement of the preservative, with the exception of that which occurs in response to a normal diffusion-surface evaporation type gradient. Cooling and/or escape of this water following treatment and exposure causes some of the preservative to move toward the center of the pole rather than toward the surface. The net result is a reduced

concentration of liquid preservative on or near the wood surface. In addition, removal of solvent by steam distillation during the final vacuum serves to further reduce the amount of preservative solution near the wood surface.

Seasoned poles contain more void space for air to occupy and to a greater depth from the surface, than similar poles treated green. When pressure is increased to force preservative into the wood, this air is further compressed and intermixed with the inflowing preservative. Subsequent release of pressure and application of vacuum relieves most of this internal pressure, but, a complete kickback is not obtained. A pressure above atmospheric still exists within the wood after release of vacuum and removal from the cylinder. The trapped air gradually works its way to the surface and pushes preservative in front of it (Thompson 1974; Kelso and Parikh 1976).

***Post treatment conditioning:*** Any successful post-treatment conditioning of seasoned southern pine poles to prevent bleeding must incorporate a period of external heating to remove any trapped air and reduce the concentration of liquid preservative near the surface (Kelso and Parikh 1976).

Kelso and Parikh (1976) evaluated weathering and preservative re-distribution on duplicate sets of green, kiln-dried and air-dried pole sections in a field test. The kiln-dried and air-dried sections were given a final conditioning by final steaming (closed) and steam distillation under vacuum. The penta gradient was determined after treatment and following exposure for 12 months and examined for evidence of bleeding. The kiln-dried and air-dried poles lost preservative from the outer zones but indicated little change in the innermost zone during the first year of exposure. There was very slight bleeding at any time after treatment and exposure and this bleeding stopped after a few days. The loss of penta from the outer zones of these sections was attributed to either to leaching and/or downward movement of preservative solution in the case of the sections exposed vertically but not to bleeding. The general absence of any persistent bleeding on the kiln-dried and air-dried sections suggests that the final conditioning procedure used; final steaming (closed) and steam distillation under vacuum with these sections was very effective. The former expels excess preservative and trapped air from the wood and the latter removes

excess water and preservative solvent from the immediate surface of the wood. The net effect of this combination is that the wood is very clean and dry when removed from the cylinder (Kelso and Parikh 1976).

***Treatment method or steps:*** The entire treating procedure should be aimed at obtaining deepest possible penetration and retentions based on service conditions and avoid overtreatment (Mayfield 1954). Preliminary vacuum is very important to reduce bleeding (Blanchard 1919). A strong vacuum drawn before and after the oil is injected will go a long way to reduce bleeding. Bleeding is significantly reduced when both steam and vacuum treatments are applied on green wood. Steaming when used without vacuum period has been shown less effective in reducing bleeding but it had more effect on tar and creosote mixture than on creosote on its own. The tar appeared to dry in the outer pores of the wood forming a mat that retarded bleeding. Insufficient vacuum after steaming leaves excess water near surface which tends to cause exudation. Quick, high initial and final vacuums of sufficient duration based on size of the charge is important. A final vacuum considerably reduces but does not completely eliminate bleeding, unless the plant is operating at very high temperatures so that the creosote has very low viscosity and the trapped air pressure can be totally relieved during the vacuum period.

Generally the higher the air pressure used in treatment the greater the bleeding. The ultimate release of the higher pressure blows more oil to and near the surface. This may not be beneficial with some thin sapwood species but the highest practicable pressure should be used (Mayfield 1954, Freeman 1988).

Initial steaming raises the temperature of the wood and reduces exudation due to reduction of viscosity of the oil, with consequent increased penetration and increased removal of oil from the outer rings of the wood. Initial steam of 1-3 hours is beneficial. Where extra cleanliness is desired a final steam, held at 240°F. for 1 -3 hrs on southern pine and 2-3 hrs on thin sapwood species is appropriate. If the initial steaming period used with green stock is insufficient, a mixture of creosote and water may exude from the

treated wood. Use of final steaming, final bath, boiling under final vacuum are beneficial as long as the retention is not reduced to an amount below that specified.

Empty cell processes generally exude less than full cell due to less concentration of oil near the surface and generally deeper penetration. Empty cell should be used when cleanliness is desired and retentions allow use, unless experimentation shows that the species being treated tends to hold air so that it escapes after treatment to cause bleeding.

Retreatment in case of inadequate penetration or retention after initial treatment should be avoided. Retreatment results in more exudation due to more preservative near the surface. Instead proper conditioning periods and suitable treatment conditions should be used to maximize retentions and penetrations in the initial treatment (Mayfield 1954).

**Temperature of preservative during treatment:** Reducing bleeding is only achieved if the preservative has low viscosity and with creosote this means heating. Keeping the temperature of the preservative during the pressure period as high as possible reduces exudation. With Creosote, Creosote-Petro solutions or highly viscous penta solutions, minimum of 200-210°F in the cylinder by end of pressure period should be used (Bergman 1991; Mayfield 1954). The heating is useless if the wood is cold or wet as the creosote will be cooled at the critical zone where it is advancing into the wood. Warming wood in a yard several days before treatment is beneficial. Hot creosote has lower viscosity, achieving both a good penetration and recovery (Richardson 1993). A study by Bergman (2003) showed that heating of the wood three hours before treatment and three hours after treatment has less bleeding even if the retention was rather high. Processes with no or only a short period of heating before pre-pressure and after oil pressure showed most bleeding even if the creosote retention was rather low.

**Storage conditions after treatment:** Poles lying on the ground show a greater amount of bleeding than the same poles after they are erected (Hatfield and Allen 1961). Material lying horizontal in storage has the sun focusing on one side all day. This may increase

bleeding as the period of storage is extended. Rotation of stock to minimize storage time, when possible is important for both penta and creosoted poles.

***Presence of sludge and Intermixing of preservatives:*** Some oil preservative solutions form true sludge reaction products due to lack of mutual solubility and through use. This insoluble material tends to filter out on the surface and cause bleeding. Maximum amount of sludge should be avoided in preservative before using it in treating wood. In treating plants which use solutions containing tar or heavy petroleum, intermixing in the cylinders and lines may cause other oil borne preservatives to pick up enough pitch and asphalt to affect bleeding appreciably. Preservatives should be kept from intermixing by using separate lines and pumps. Systems that will drain completely help to prevent intermixing. Keep the cylinder clean.

If all the above strategies if the treatments result in a reduction of retention to less than specified, there will be reduction in service life. If, however, the retention is according to the specifications and the highest concentration of preservative is only removed to a point inside the wood, the service life might actually be increased due to a reduction in the loss from the wood, caused by a high concentration at the surface (Mayfield 1954).

## **RESEARCH TO REDUCE BLEEDING OF CREOSOTE**

A survey of the eleven papers presented before the American Wood- Preservers' Association from 1911 till 2005 shows that bleeding has been a subject of interest since 1915. Since then, various authors have stressed the importance of wood processing steps, necessity of using a proper preservative formula or type. Research on formulation has addressed concerns about appearance, smell, and handling characteristics of creosote. In 1926 an author reported that the use of montan wax, after a regular treatment with creosote reduced bleeding and evaporation (Hatfield and Allen 1961). In 1934 the addition of phosphatide (lecithin) to commercial creosote, was suggested as a means of improving the distribution of the preservatives in the sapwood, making it more uniform than in an ordinary empty-cell treatment. The heavy concentration of the oil in the outer annual

rings is reduced, and the tendency of the poles to bleed is reduced. Poles and cross-arms treated with this process showed that less than 1 percent of bleeding has been encountered, and more than 90 percent of the poles showed no bleeding (Hatfield and Allen 1961).

Laboratory studies dealing with the addition of 1-2% low melting point waxes or polymer solutions to petroleum oil solutions containing penta, indicated that they lowered the threshold concentration of preservative required to control decay fungi. With penta petroleum solutions bleeding was reduced by 50-88% and at least 50% for creosote. Higher concentration of effective additives in either penta or creosote could cause operational difficulties, affect distribution and retention as well as be excessive in cost, so the work was aimed at finding an additive that would perform at these low levels of concentration. Several polymers and copolymers were screened for this application. No commercial processes currently report the used of the processes above.

In more recent years, In the US creosote-treated products exhibiting cleaner dried surfaces and reduced bleeding have been achieved through reduction of the xylene-insoluble carbonaceous fraction in creosote. In Australia, pigment-stabilized creosote emulsion formulations have been developed to lock the oil phase within the treated timber. The surfaces of PEC-treated wood remain dry, and the oil remains mobile within the microstructure. Treatment of wood with PEC 30W is generally comparable to treatment with reference creosote PI/P13, except that slightly greater variability in creosote loading occurs with PEC. The PEC formulation was developed and is used in Australia (Crawford et al., 2000).

## **SUMMARY AND CONCLUSIONS**

Bleeding of all oil-borne/oil type wood preservatives has been any issue since the early 1800's. The general conclusions are that most bleeding is due to entrapped oil in the wood cells, and upon expansion or relaxation, the oil trapped inside the wood forces the oily preservatives to the surface. Historically, copper naphthenate has shown less bleeding than either creosote or pentachlorophenol solutions or treated wood; this phenomena may

be due to it being a lesser used product over the last 4 decades and that the treaters using this product have usually be those treaters classified as the most caring about appearance. Slumping, or the movement of oil borne preservatives due to gravity, from an upper position, as in poles, to the groundline is beneficial and not considered a detriment to the treatment, but an advantage, as long as the oil around the pole base is not excessive. Many processes can be employed to minimize bleeding, and included in those processes are items such as extended final vacuum, longer expansion baths, efforts to slow thru-plant processing of poles, and final steaming. Generally all bleeding can be controlled by the wood treater and is generally not thought to be a characteristic of the treating solution itself.

## References

Bergman Ö 1991. Temperature and pressure inside wood during creosote impregnation. Int. Res. Group on Wood Protection. IRG/WP 3649.

Bergman Ö 2003. Influence of different treatment parameters on penetration, retention and bleeding of creosote. IRG/WP 03-40255.

Richardson BA. 1993. Wood preservation. 2nd Edition.

Blanchard AH. 1919. American highway engineers' handbook.

Crawford, D.M., DeGroot, R.C., Watkins, J.B., Greaves, H., Schmalzl, K.J. and Syers, T.L. 2000. Treatability of U.S. wood species with pigment emulsified creosote. Forest Products Journal 50 (1).

Chakraborty A. 2001. Investigation of the loss of Creosote components from railroad ties. MS. Thesis. Department of Chemical Engineering and Applied Chemistry. University of Toronto.

Hatfield I and Van Allen RG. 1961. Reducing Oil and Oil-Borne Preservative Losses from Wood Through the Use of Preservative Stabilizers. Proceedings AWWA 1961.

Ibach, R.E. 1999. Wood preservation. In Wood handbook—Wood as an engineering material. Chapter 14. Forest Products Laboratory. Gen. Tech. Rep. FPL–GTR–113. Madison, WI.

Johnson, GC and Thornton, JD. 2000. An Australian test of wood preservatives. IV. The condition, after 35 years' exposure, of stakes treated with creosote oils and oilborne preservatives. Int. Res. Group on Wood Protection. IRG/WP 00-30241.

Kelso WC and Parikh SV. 1976. Study of the Factors Influencing the Color and Bleeding Characteristics of Southern Pine Poles treated with Penta. in Hydrocarbon Solvent. AWWA. 99.

Lebow ST. and Tippie M. 2001. Guide for Minimizing the Effect of Preservative-Treated Wood on Sensitive Environments. General Technical Report. FPL-GTR-122.

Leutritz J. 1957. Bleeding of oil Preservatives. Bell laboratories record.

Mayfield PB. 1954. The exudation of oil-type preservatives from treated wood. J. Forest Prod. Res. Soc. 4(1): 52-55.

Melber C, Kielhorn J and Inge Mangelsdorf I. 2004. Coal Tar creosote. Concise International Chemical Assessment. Document 62. World Health Organization.

Scheffer TC., Miller DJ and Morell JJ. 1997. After 18 years, preservative Dipping and Brush treating continue to provide protection to shingles of western wood species. Int. Res. Group on Wood Protection. IRG/WP 97-30156.

Thompson JB. 1974. A preliminary report on bleeding of pressure treated southern pine poles, pp. 163-168. Report of AWPA Committee T4-Poles. Proceedings AWPA. 70:153-172.

Wacker JP, Crawford DM, Eriksson MO. 2003. Creosote retention levels of timber highway bridge superstructures in Michigan's lower peninsula. Res. Note FPL-RN-0289. Madison, WI: USDA. Forest Products Laboratory. 17 p.

Walters, CS. and Arsenault RD. 1971. The concentration and distribution of pentachlorophenol in pressure-treated pine pole-stubs after exposure. Proceedings AWPA. 67: 149-169.