Termogravimetrik Verilerden Borik Asitin Dehidratasyon Kinetiği
Dehydration Kinetics Of Boric Acid Using Thermogravimetric Data

F. Sevim, H. Okur & F. Demir
Atatürk Üniversitesi, Mühendislik Fakültesi, Kimya Bölümü, 25240, Erzurum TURKEY.
A. Mergen & M. Bilen
Eti Holding A.Ş., Ar-Ge Dairesi Başkanlığı, İstanbul Yolu Üzeri, 9 km, Güvercinlik, Ankara TURKEY.

ÖZET: Bu çalışmada, borik asidin termal ayrışmasının kinetik parametreleri TG datalan kullanılarak İncelenmiştir. Kinetik analiz için Suzuki ve Coats-Redfern metotları uygulanmıştır. Borik asidin aynşma kinetiğinin iki kademe halinde meydana geldiği ve her iki bölgede de birinci mertebe kinetik modele uyduğu belirlenmiştir. Aktivasyon enerjisi değerleri I. Bölge için 79.85 kj.mol^1 ve II. Bölge için 4.79 kj.mor^1 ve frekans faktörleri, I. Bölge için 3.82xl0^4 ve II. Bölge için 4.045xl0"^{5} olarak hesaplanmıştır.

ABSTRACT: In the present study, the kinetic parameters of thermal decomposition of boric acid was examined using TG data. Suzuki and Coats-Redfern methods were applied for the kinetic investigation. It was determined that decomposition kinebcs of bone acid was occured in two steps and both regions were suitably fit with first degree kinetic model. Activation energies and frequency factors were determined respectively as 79,85 kjmol"^{1} and 3,82xl0^4 for the first region and 4,79 kj-mol"^{1} and 4,04x10^s for the second region.

1 GİRİŞ

Türkiye, dünyadaki bor rezervlerinin %63 gibi büyük bir kısmına sahiptir. Tinkal, kolemanit ve üleksit gibi pek çok önemli bor yatakları Türkiye'ce bulunmaktadır. Türkiye'de bulunan bor yutakları Eti Holding A.Ş.'ye bağlı Eti Bor A.Ş. tarafından işletilmekte ve çıkanlan bor cevherlerinden, bor konsantrelen ve bunlardan da rafine bor Ürünleri elde edilmektedir. Tablo l'de Türkiye'de üretilen bor konsantreleri, rafine bor ürünleri ve üretildikleri bölgeler verilmiştir. Türkiye'de borik asit üretimi Bandırma'da bulunan Eti Bor A.Ş. 'ye bağlı Bor ve Asit Fabrikalan İşletme MüdÜrlUğü'nde kolemanit konsantresi ve sülfürik asit kullanılarak gerçekJeştnilmektedir.

Bandırma'da üretilen borik asitin safiyeti %99,9 olup, sülfat içeriğine göre borik asit normal sülfatıı (130-500 ppm SO* içermektedir) ve düşük sülfatıı (maksimum 130 ppm SO« içermektedir) olarak iki kategoride ele alınmaktadır

Borik--asit, bir çok sektörde geniş kullanım alanlarına sahiptir. Borik asit, cam ve seramik endüstrisinde, tarımda gübre olarak, selülozîk maddelerde alev geciktincı olarak, nükleer uygulamalarda, bor alaşımlarında, tekstil sektöründe ve daha bir çok alanda kullanılmaktadır (DPT, 2001).

Farklı yöntemler kullanılarak literatürde bazı bor minerallerinin ve rafine bor ürünlerinin termal aynşma reaksiyonlan incelenmiştir. Şener ve arkadaştan (Şener ve arkadaştan, 2000) tarafından yapılan çalışmada üleksitin termal aynşma reaksiyonlarının mekanizması ve tabiatı TG, DTA ve DTG ile belirlenmiş ve üleksitin yapısında meydana gelen değişiklikler XRD, SEM ve civa porozimetresi ile İncelenmiştir, incelemeler sonucunda üleksit yapısında meydana gelen değişiklerin iki aşamada gerçekleştiği gözlemlenmiştir. 60-500°C aralığın- daki birinci bölgede, yapı önce 180°C'ye kadar $NaCaB_5O_6(OH)_6$. SFfcO'ya daha sonra 151-260°C*de $NaCaB506(OH)6.H_2O$'ye dönüştüğü tespit edilmiştir. 260-500°C sıcaklık aralığında ise

üleksit bünyesinde kalan hidroksil gruplarının uzaklaştığı saptanmıştır (Şener ve arkadaşları, 2000).

Üleksıtm termal bozunmasıyla ilgili olarak yapılan diğer bir çalışmada (Tunç ve arkadaşları, 1997), üleksitin termal ayrışması kinetik parametreleri, TGA dataları kullanılarak Suzuki ve Coats-Redfem metotlarının uygulan-masıyla incelenmiştir. Aynşmanın iki bölgede meydana geldiği ve her iki bölgedeki ayrışmasında 1. mertebe kinetik modeline uyduğu bulunmuştur. Üleksit tane boyutunun azalmasıyla aktivasyon enerjisinin ve frekans faktörünün azaldığı belirtilmiştir (Tunç ve arkadaşları, 1997).

Diğer bir çalışmada (Şahin ve arkadaşları, 2001) ise, amonyum pentaboratm TG verilerinden kalsinasyon kinetiği Coats-Redfern ve Genetık-Algontma metotları kullanı-larak araştın Imıştır. Bu çalışmada, aktivasyon enerjisi, frekans faktörü, reaksiyon mertebesi ve bunların nispi standart sapmalarının tespiti için genetik algoritma yöntemi uygulan-mıştır. Reaksiyon parametreleri benzer şekilde Coats-Redfem metodu ile hesaplanarak elde edilen sonuçlar her iki metot için karşdaştınlmıştır (Şahin ve arkadaşları, 2001).

Bonk asit üretimi için yapılan bir çalışmada (Davies ve arkadaşlan, 1991); toz halindeki kolemanite kalsinasyon ve lıç yöntemleri uygulanmıştır. Bu çalışmada, kalsinasyon için 600°C* de klasik (soak) ve flash kalsinasyon metotları uygulanmış ve elde edilen sonuçlar birbirleriyle mukayese edilmiştir. Daha kısa sürede gerçekleşen flash kalsinasyonda asit liçine yüksek dirençli ve daha gözenekli bir yapı elde edilmiştir. Elde edilen kalsine ürün, farklı liç parametreleri kullanılarak incelenmiştir (Davies ve arkadaşlan, 1991)

Tablo 1 Etı Holdmg A Ş 'ye bağlı Etı Bor A Ş tarafından üretılen bor konsantrelerı ve rafine bor ürünlerı

	Üretimin Yapıldığı Yer	B₂O₃ (%)
Bor Konsantresi		
Tınkal Konsantresı	Kırka	32
Kolemanıt Konsantresı	Emet, Bigadıç*, Kestelek	36-42
Üleksıt Konsantresı	Bıgadiç	25-38
Rafine Bor Ürünlerı		
Boraks Pentahıdrat	Kırka, Bandırma	47,7 (mın)
Boraks Dekahıdrat	Kırka, Bandırma	36,47 (mın)
Susuz Boraks	Kırka	68,87
Borik Asıt	Bandırma	56,25 (mın)
Sodyum Perborat	Bandırma	22,6 (mın)

* Bigadiç*de üretilen konsantre koüemaoıtın yüzde B3O3 içengı 27-42 aralığındadır

Kot Kırka Eskişehir ılı ne, Emel Kütahya iline, Bigadiç ve Bandırma Balıkesir ilme, Kestelek Bursa iline bağlıdır

Borik asit yavaş ısıtıldığı zaman suyunu kaybederek metaborık asİte dönüşür (Kirk-Othmer, 1990). Metaborik asidin 3 ayrı kristal modifikasyonu vardır.

Ortorombık metabonk asit : $(HBO_2-IU$, ergime noktası= 176°C),

Monoklınık metaborık asit: (HBOa-n, ergime noktası= 200.9°C),

Kübik metabonk asit. $(HBO_2-I$, ergime noktası= 236°C)

Sıcaklık 150°C'in üzerine çıkmadığı sürece dehidrasyon HBO_2 formunda kalır. Daha yüksek sıcaklıklarda borik asit bünyesindeki tüm su uzaklaşarak susuz borik asit elde edilir. Kristal susuz borik asit 450°C de ergir. Amorf susuz borik asit belli bir ergime derecesine sahip değildir. Yakıaşık 325°C de yumuşamaya başlar ve yaklaşık 500°C de tamamen akışkan hale gelir (Kocakuşak ve arkadaşlan, 1998).

Bonk asidin (H_3BO_3) tamamen aynşması sonucunda bor oksit (B_2O_3) oluşur. Fiziksel ve kimyasal özelliklerinden dolayı bor oksidin çok farklı kullanım alanları mevcuttur. Bor oksit en fazla inorganik ve organik bor bileşiklerinin üretiminde başlangıç hammaddesi, pek çok organik maddenin üretiminde de katalizör, metalürji sanayiinde flaks olarak kullanılır. Belirtilen uygulamalara ilave olarak bonk asit; cam, cam elyafı, optik elyafı, seramik, metal kaplama, bor aiaşunlan, elektronik sanayii, alev geciktiricilerde de kullanılır.

Yapılan bu çalışmada, borik asidin termal ayrışmasının kinetik parametreleri TG dataları kullanılarak Suzuki t Suzuki ve arkadaşlan, 1978) ve Coats-Redfern (Coats ve Redfern, J964)

metotlarıyla incelenmiştir. Bandırma Bor ve Asit Fabrikalarında üretilen borik asidin tane boyutu 0,06-1 mm arasında standart olması nedeniyle bu çalışmada borik asit tane boyutunun etkisi incelenmemiştir. Çalışmamızın amacı (İlkemizde üretilen bor cevherlerinin değerlendirilmesi açısından Önemli olup, literatür araştırmalarımızda böyle bir çalışmaya rastlanmamıştır.

Bu çalışmada, borik asidin termal ayrışmasının kinetik parametrelerinin bulunmasına yönelik olarak kullanılan Suzuki (Suzuki ve arkadaştan, 1978) ve Coats-Redfem (Coats ve Redfem, 1964) metotlarıyla ilgili teorik kısım aşağıda verilmiştir.

2. TEORİK KISIM

2.1. Coats-Redfem Metodu

Bu metotta, katı bir maddenin bozunma reaksiyonu katı maddenin termal bozunması olarak tanımlanabilir. Reaksiyonun bu tipi aşağıdaki gibi gösterilebilir.

$$aA_{katı} \longrightarrow bB_{katı} + cC_{gaz} \qquad (1)$$
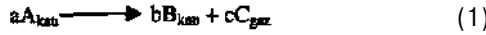
Katı maddenin bozulma hızı, $A_{katı}$ denklemdeki gibi ifade edilir.

$$\frac{dx}{dt} = k(1-x)^n \qquad (2)$$

Burada x dönüşüm kesri, t zaman, k hız sabiti ve n reaksiyon mertebesıdır.

Isıtma hızı q = dT / dt, ve hız sabiti k=koexp(-E/RT) yerine konarak eşitlik tekrar yazılırsa

$$\frac{dx}{dt} = \frac{k_o}{q}(1-x)^n \exp\left(\frac{-E}{RT}\right) \qquad (3)$$

burada k« frekans faktörü, T mutlak sıcaklık, E aktivasyon enerjisi ve R Universal gaz sabitidir. Eşitlik (3) dönüşüm kesri için 0 ile x arasıda ve sıcaklık için T_0 İle T sınır şartlarında integral alınırsa aşağıdaki ifade elde edilir.

$$\frac{1-(1-x)^{1-n}}{(1-n)} = \frac{k_o}{q}\int \exp\left(\frac{-E}{RT}\right)dT \qquad (4)$$

Eşitliğin sağ tarafı tam integral değildir, fakat aşağıdaki eşitlik, eşitliğin sağ tarafı bir asimtotik seriye açılarak elde edilir ve daha yüksek terimleri dikkate alınmaz.

$$\frac{1-(1-x)^{1-n}}{T^2(1-n)} = \frac{k_o R}{qE}\left(1-\frac{2RT}{E}\right)\exp\left(\frac{-E}{RT}\right)(n\neq 1) \quad (5)$$

Burada kJR/qE , ısıtma hızının ve herhangi bir tanımlı n'nin değeri İçin sabittir. RT/E « 1, kabul edilirse, Eşitlik (5) aşağıdaki gibi kısalır,

$$\frac{1-(1-x)^{1-n}}{T^2(1-n)} = \frac{k_o R}{qE}\exp\left(\frac{-E}{RT}\right) (n\neq 1) \qquad (6)$$

n=l için, Eşitlik (3) ten aşağıdaki denklem aynı kabulle elde edilir:

$$\frac{-\ln(1-x)}{T^2} = \frac{k_o R}{qE}\exp\left(\frac{-E}{RT}\right) (n=1) \qquad (7)$$

Aşağıdaki fonksiyonlar tanımlanırsa genel denklem yazılabilir

$$f(x) = \frac{1-(1-x)^{1-n}}{(1-n)} \quad (n\neq 1) \qquad (8)$$

$$f(x) = -\ln(1-x) \quad (n=1) \qquad (9)$$

Aşağıdaki genel eşitlik yazılabilir.

$$\ln\frac{f(x)}{T^2} = \ln\left(\frac{k_o R}{qE}\right) - \left(\frac{-E}{RT}\right) \qquad (10)$$

$ln(f(x)/T^2$ karşı l/T eğrisi eğimi -E/R 'dir. Frekans faktörünün değeri bu doğrunun eğiminden hesaplanır [8].

2.2. Suzuki Metodu

Bu metotta TG verilerinden elde edilen sıcaklığa karşı dönüşüm eğrisi kinetik parametreleri elde etmek için kullanılır. %50 dönüşüme karşılık gelen sıcaklık, T m , ve %50 dönüşüm noktasındaki eğrinin eğimi olan A7] bu eğri kullanılarak bulunur. Aşağıdaki fonksiyon aşağıdaki denklemle tanımlanırsa

$$\xi = \frac{\Delta T}{T_{1/2}} = \frac{2}{\ln 2}\varphi\left(\frac{E}{RT_{1/2}}\right) \qquad (11)$$

burada

$$\varphi\left(\frac{E}{RT_{1/2}}\right) = 1 - \left[ze^z E_1(z)\right] \qquad (12a)$$

$$E_K(z) = \int\limits_0^\infty \left[\frac{exp(-z)}{z} \right] dz \qquad (12b)$$

$z=E/RT//2$, T prosesin aküvasyon enerjisini hesaplamak için, E, sıcaklığa karşı dönüşüm eğrisinden elde edilir, ve a terimi Eşitlik (ll)'den hesaplanır, z değerinin tahmini için Suzuki tarafından hazırlanan grafik kullanılır. Frekans faktörü aşağıdaki eşitlikten hesaplanır [9].

$$k_0 = \frac{2q}{\Delta T} exp\left(\frac{E}{RT} \right) \qquad \qquad (13)$$

3. DENEYSEL ÇALIŞMALAR

Mevcut çatışmada kullanılan borik asit, Bandırma Bor ve Asit Fabrikalarından elde edilmiştir. Borik asidin kimyasal analizi Tablo 2'de verilmiştir. Kullanılan borik asidin tane boyutu 0,06-1 mm arasındadır. Borik asidin bozunma reaksiyonları SETARAM Labsys 3.0 DTA-TGA sistemi kullanılarak gerçekJeştirilnustir. DTA-TG deneylen platin bîr kroze içerisinde, 3°C/dak. ısıtma hızında ve azot atmosferinde gerçekleştirilmiştir. Yapılan deneyler neticesinde elde edilen DTA-TG grafiği Şekil 1'de sunulmuştur.

Tablo 2. Borik asidin kimyasal analizi

Borik Asit	
B_2O_3	% 56,27
SO_4	190 ppm
Na	50ppm
Ca	50 ppm
F«	20 ppm
Al	20 ppm
SiQ_2	40 ppm
Mg	270 ppm
K	20 ppm
Pb	9 ppm
Li	İ ppm
Cu	4ppm
Co	1 ppm
Ni	4 ppm
Mn	6 ppm
Cr	S ppm
Sr	1,5 ppm

4. SONUÇLAR VE TARTIŞMA

Şekil 1 de verilen DTA ve TG eğrilerinden elde edilen r-kare değerlerinin 1. mertebeye uyduğu bulunmuştur. Borik asidin DTA eğrisinde iki endotermik pik gözlenmiştir. TG eğrilerinde görüldüğü gibi sıcaklık arttıkça kütle kaybı da artmaktadır. Dönüşüm kesri, işlemin sonundaki toplam kütle kaybı ile verilen sıcaklıktaki kütle kaybına oranı ile bulunmuştur. Kinetik parametre-lerin belirlenmesi için, Coats-Redfern ve Suzuki metotları denenmiş ve karşılaştırılması yapılmıştır. Bu iki metoda göre, Coats-Redfern metodunun her İki bölgeye ayn ayrı uygulanabilmesinden dolayı Suzuki metoduna göre daha iyi sonuç verdiğine karar verilmiştir.

Ağırlık kaybını içeren katı hal reaksiyonlarının kinetik parametrelerinin değerlendirilmesi için termogravimetrik verilerin kullanımı çeşitli metotlarla yapılabilmektedir. Bu çalışmada, bunlardan biri olan Coats-Redfem metodu $aA—*bB+cC$ şeklindeki bîr denklemin kinetik parametrelerini belirlemede kullanılmıştır. Reaksiyon mertebesi $ln(f(X)/T^2)$ karşı (l/T) çizilen grafikten hesaplanmıştır. Şekil 2'den görülebi-leceği gibi bu metoda göre kinetik parametrelerin hesaplanmasında 2 farklı bölgenin dikkate alınması daha uygun olacaktır. Bu nedenle her iki bölge için ayn ayn çizilen Şekil 3 ve 4 dikkate alınarak, teorik kısımda belirtilen denklemlere TG venleri uygulanmıştır. Metot uygulandığında, ağırlık kaybı 3-28 arasında olan yani sıcaklık aralığı 11S-162°C bir bölge ve ağırlık kaybı 28-43,15 arasında olan yani sıcaklık aralığı 162-430°C ikinci bölge için hesaplamalar yapılmıştır. Birinci bölgenin 1. mertebe kinetik modele uyduğu ve aküvasyon enerjisi ite frekans faktörünün sırasıyla 4,79 kj/mol ve 4,04x1 tT^s olduğu hesaplanmıştır, ikinci bölgenin de 1. mertebe kinetik modele uyduğu ve aktivasyon enerjisi ile frekans faktörünün sırasıyla 79,85 kj .mol"¹ ve 3,82x 10* olduğu hesaplanmıştır. Denenen diğer mertebeler ve r-kare değerleri Tablo 3'de verilmiştir. Bu verilere göre borik asidin dehidrasyomu aşağıdaki şekilde gösterilen iki kademeli reaksiyonla meydana geldiği düşünülebilir.

$2H_3BO_3 -» 2HBÛ2 + 2H_2O$ (1. Bölge)
$2HBO_2 -» B2O3 + H_2O$ (2. Bölge)
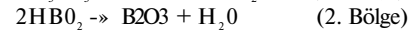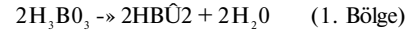
Suzuki metodunu uygulamak için sıcaklığa karşı dönüşüm kesrinin eğrileri Şekil 5'de gösterildiği gibi çizilmiştir. 4 sıcaklığa karşı dönüşüm eğrisinden elde edilirken, <p terimi eşitlik 11 kullanılarak hesaplanmıştır, z değerinin tahmini Suzuki [9] tarafından hazırlanan grafik kullanılarak yapılmıştır. Frekans faktörü eşitlik 13'den elde edilir. AT ve Tl/2 nin değerleri bu eğrilerden sırasıyla 426 ve 52,7 K olarak elde edilmiştir. Suzuki metoduna göre aküvasyon enerjisi

4,45 kj.mo] ' ve frekans faktörU 4,08x10* olarak hesaplanmıştır.

5. KAYNAKLAR

Coats, A.W. ve Redfern, J.P, 1964. Nature, 201, 68.

Davies, T.W., Çolak, S. ve Hooper, R.M., 1991. Bone Acid Producting by the Calcination and Liçing of Powdered Colemanıte, Powder Techonology, 65,433-440

DPT, 2001. VIII. Beş Yıllık Kalkınma Planı, Madencilik (Endüstriyel Hammaddeler: Kimya Sanayii Hammaddeleri) Cilt II, Ankara, DPT.

Kırk-Othmer Encyclopedia of Chemical Technology, 1990. Vol. 1, No:4, Smith, R., Boric Oxide, Boric Acid, and Borates.

Kocakuşak, S., Akçay, K., Ayok, T., Köroğlu, J., Savaşçı, T. ve Tolun, R., I 998 Akışkan Yatakta Bor Oksit üretim Teknolojisinin Geliştirilmesi, Tıibitak Araştırma Merkezi, Rapor No: KM 323.

Suzuki, M., M\sıc,D,M., Koyama, O ve Kawazoe, K-, 1978. Study of Thermal Regeneration of Spent activated Carbons: Thermogravimetnc Measurement of Various single Component Organics Loaded on Activated Carbons, Chemical Engineering Science, 33, 271-279.

Şahin, ö., Özdemir, M., Aslanoğu,M, ve Beker, Ü G., 2001. Calcination Kinetics of Ammonium Pentaborate Using the Coats-Redfern and Genetic Algorithm Method by Thermal Analysis, Ind. Eng. Chem. Res, 40, 1465-1470.

Şener, S., Özbayoglu, G. ve Demirci, Ş., 2000. Changes in The Structure of Ulexite on Heating, Thennochimica Acta, 362,107-112-

Tunç, M., Erşahan, H., Yapıcı, S. ve Çolak, S., 1997. Dehydration Kinetics of Ulexite From Thermogravimetnc Data, Journal of Thermal Analysis, 48,403-411.

Sembollerin Açıklanması

Semboller	Anlamlan	Birimi
E	Aküvasyon Enen J sı	Ki mor^1
k	Hız Sabıü	s^{n1}
K	Frekans Faktörü	s^1
n	Reaksiyon Mertebesi	
o	İsıtma Hızı	Ks-^{1}
R	Universal Hız Sab\U	83\4kıınol'lC
T	Sıcaklık	K
x	Dönüşüm Kesn	

Tablo 3. Coats-Redfera metoduna göre elde edilen r-kare değerlen

Mertebe	1. bölge r-kare	2.bölge r-kare
1. Mertebe	0.961348	0,999833
0. Mertebe	0,941641	0,994723
1/3. Mertebe	0,864612	0,99745
1/2. Mertebe	0.724741	0,99842
2/3. Mertebe	0,094047	0.999136
3/4. Mertebe	0,298898	0,9994
3/2. Mertebe	0,950236	0,999187
2. Mertebe	0,934719	0,996792
5/2. Mertebe	0.929999	0.993012
3. Mertebe	0.929475	0,98822
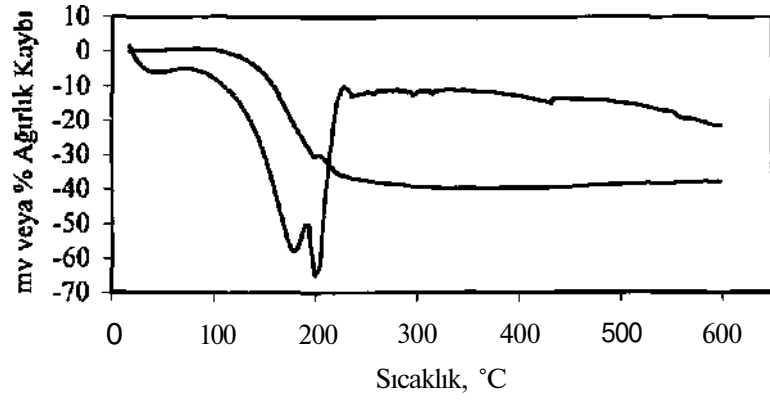
Şdcı M   Bonk asidin DTA-TG grafiği
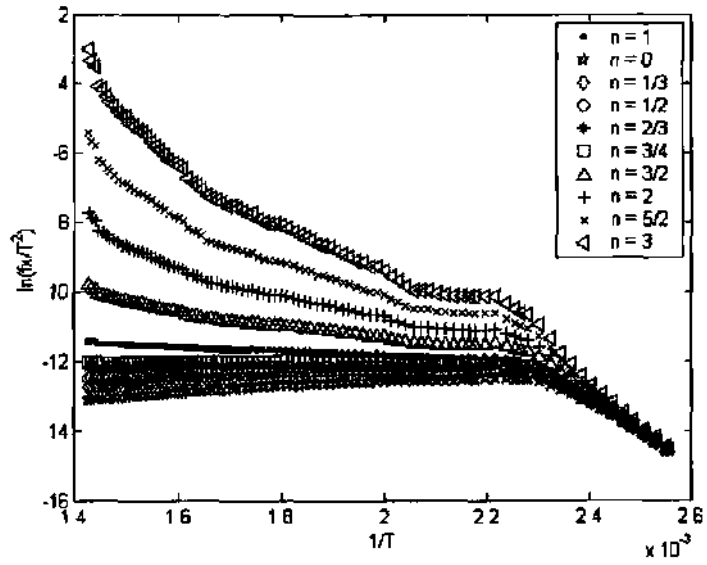
Şekil 2 Bonk asidin dehjdrasyonu ıçm Coats-Redfern metodunun davranışı
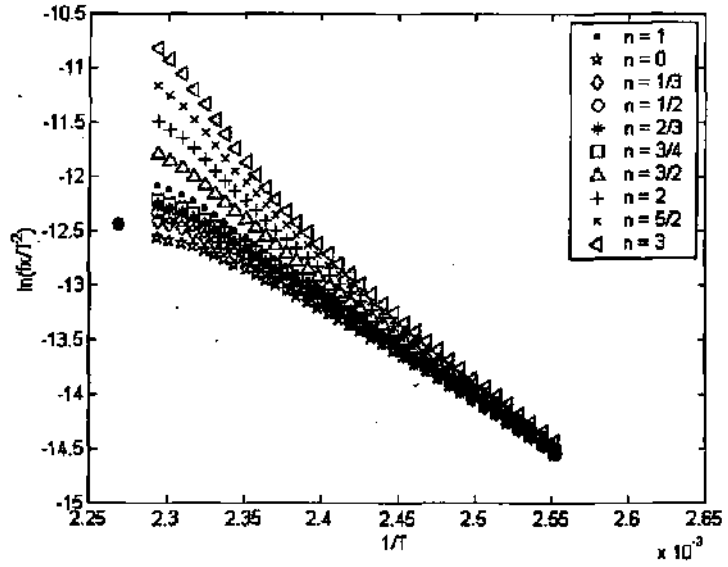
Şekil 3. Coats-Redfern metoduna göre 1. Bölge için mertebelerin denendiği grafik
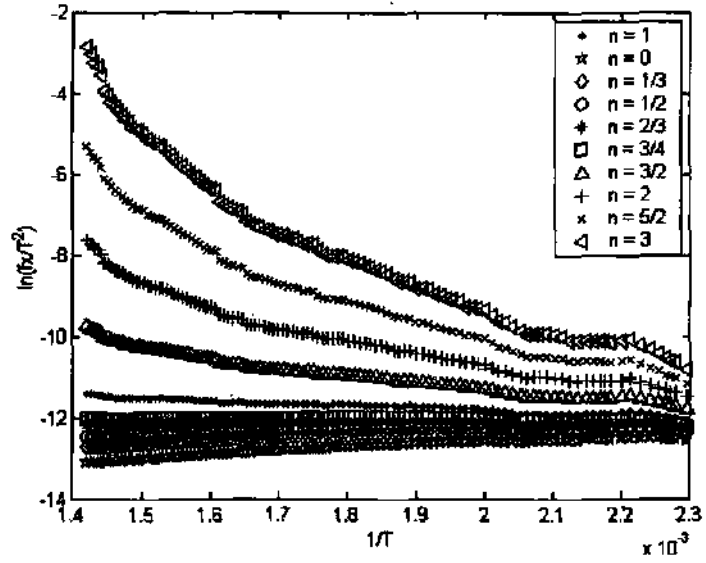
Şekil 4. Coats-Redfern metoduna göre 2. Bölge için mertebelerin denendiği grafik

90

Şekil S   Suzuki metoduna göre TG verilerinden eide edilen grafik

A comparative study on stability and decay resistance of two environmentally friendly fire-retardant boron compounds: PHN 130 and PHN 130G

M.K. Yalınkılıç & E.Baysal
Furniture & Decoration Descıplıne, Technical Education Faculty, Muğla University, Muğla, TURKEY
Y.Imamura
Wood Research Institute, Kyoto University, Uji, Kyoto, 611, JAPAN

ABSTRACT: Environmental concern accelerated development of new wood preservatives having low mammalian toxicity in addition to high protective effectiveness. PHN 130 and PHN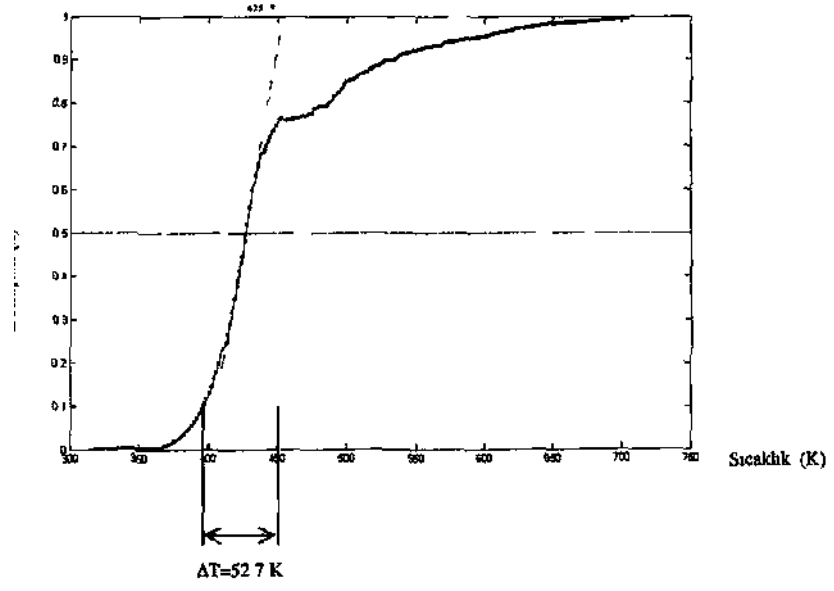 130 G have been developed recently by KOHMIX Ltd. in Japan, •as "environmentally safe", fireproof boron containing compounds. Beyond their proved fire-proof properties, stability of loaded chemical in wood at humid service conditions and decay resistance are required to be known for effective and broad use of these compounds in wood preservation.
Results indicated that PHN imparted complete decay resistance to wood against brown-and wbite-rot fungi *Tyrornyces palustris* and *Coriolus versicolor,* respectively. Protection efficacy of PHN also continued despite severe weathering conditions provided that impregnation is done by undiluted solution PHN 130 G appeared more effective than PHN İ30 İn dûs respect. However, both compounds were leachable from treated wood regardless to retention level or physical restriction of water access into wood by compression.

1. INTRODUCTION

A treatment for wood, the water-soluble borates combine a unique set of characteristics: efficacy as a preservative against fungi and insects, fire retardancy at higher loading, low cost, ease of handling and treatment, low mammalian toxicity, a minimal environmental impact (Laks & Palardy, 1990) Different levels of boron retention is necessary for biological activity against decay fungi and insects and for fire resistance. Around 1 % w/w *(2.5* kg/ra³) boric acid (BA) loading was found sufficient for decay resistance against *Tyrornyces palustris* and *Coriolus versicolor,* representing brown- and white-rot fungi, respectively, while about 17 times higher loading as 17 % w/w (42-2 kg/rn³) necessitated for total inactivation of Formosan subterranean termite *Coptotermes formosanus* Shİraki (Yalinkılıç et al-, 1996). On the other hand, although loading levels for biological resistance can contribute to fire retardancy (Yalinkılıç

et al., 1997a), more than 48 kg/rn³ borax (BX)-BA mixture is necessary to required level of fire resistance designated Class I at ASTM E 84 (Levan & Tran, 1990; ASTM, 1988). However, bone compounds are within the limits of dilute concentration resulting in their limited fire-proof performance.

In a recent progress to achieve effective boron-based fire-retardant formulations, two compounds were developed by KOHMIX Co. Ltd. (Japan) and marketed as "liquid ceramics and silanol salt type MF, and acid type PHN (KOHMIX, 1996). The latter consists of BX and BA mixture accompanied by a chelating agent and a surfactant. The invention of PHN had been based on obtaining fire-proof and fire-resistant composites containing concentrated boric compounds to make wood or other natural fibers resistant against fire without evolving hazardous gas and fume when set on fire. Combination of BA with BX is generally preferred

to counteract the poor suppression effect of BX on glowing [(Yalinkiliç et al.. 1997; Arthur& Quill, 1992). Acidity of die mixture was set to 6 by an another fire-retardant; phosphoric acid (PA). As a flame retardant, PA contributes to fire resistance by reducing pyrolysis temperature and amount of flammable volatiles and, increasing amount of char and preventing glowing combustion (Browne& Tang, 1962; Browne, 1958; Lyons, 1970; Ellis, 1991). In addition, PHN has no side effect on material's strength owing to its mild pH level (KOHMIX, 1996). Solubility of BX and BA in water increased from 5 % to 70 % or more at 20 °C with this new combination, and so much as 120 g/100 ml water solubility became available at 50 °C or at higher temperatures. Standpoint of the product development was to load the more chemical into wood through impregnation with concentrated treatment solution at ambient temperature. Absorption of 200 to 250 kg liquid PHN per cubic meter wood was found sufficient in order to make it incombustible. In the present use, PHN is mixed with used newspaper shreds together with a synthetic resin prior to hot pressing of mat to obtain recycled fire-proof-composite board. Mixing to other lignocellulosic fiber sources to manufacture either medium density fiber board (MDF) or particleboard, and coating over paper or board surface are also suggested among many other potential fireproof applications of PHN (KOHMIX, 1996). In addition to more boron deposition in wood to obtain flame-resistance, PHN is also expected to impart wood a certain level of biological resistance against decay fungi and destroying insects owing to the bioactive nature of boron. However, chelate complexion inhibits the bioacnvity of boron in certain combinations, although stabilizes it in wood (Lloyd et al., 1990; Lloyd, 1993). Because enzyme assays along with fungal growth experiments led to the hypothesis that complex formation of "free" borate ion may have an adverse effect on toxic mechanism of boron compounds (Lloyd et al., 1990; Lloyd, 1993; Nicholas et al., 1990). On the other hand, because of readily leachable character of water soluble boron salts from treated wood, they are not usually preferable for treatment of the timber to be used at ground contact or outdoor exposure conditions (Yalinkiliç et al., 1996; Nicholas et al., 1990; Yalinkiliç et al., 1997b) . Biological activity against decay fungi and stability of PHN at humid service condition are, therefore, required to be known to ascertain its effective and broad use in wood preservation.

Recently, teachability of boron could be delayed to a considerable extent by compression of BA treated wood under heating aimed at recrystallization of boron into more stable forms and reducing water access in wood (Yalinkiliç et al., 1999). Taking account this and phase transition property of PHN into solid upon dehydration at high temperatures to form a heat resistant ceramic film without disintegration (KOHMIX, 1996), PHN treatment was incorporated with the compression process of wood under hot press. Thus, the present study dealt with the teachability of boron from uncompressed- and compressed-PHN treated wood and decay resistance before and after cyclic weathering.

2. MATERIALS and METHODS

2.7. *Chemicals and treatment conditions*

Wood specimens measuring 20 (T) x 20 (R) x 10 (L) mm were prepared from air-dried sapwood of Japanese cedar *(Cryptomeria japonica* D. Don) wood. Specific gravity was 0.34, based on the measurements of hundred specimens selected randomly. Two boron containing commercial compounds PHN 130 and PHN 130 0 were used at impregnation. 10 % and 50 *%* (w/w) aqueous solutions and, undiluted ready-to-use solutions of these PHN types supplied by KOHMIX Co. Ltd. were impregnated into wood in a treatment chamber by applying 30 mm vacuum of specimens at 760 mmHg' followed by leaving in the treatment solution for 30 mm for diffusion. Treatments were duplicated under identical conditions.

Weight gain of the specimens due to PHN loading was calculated from the initial and final oven dry weights as follows;

Weight gain (*, Wl w) = [(W* W,,) / W_dJ x 100 (1)

where, W,,r is the final oven-dried weight of a specimen and W,, is that of the initial.

On the other hand, bulking efficiency of loaded chemical was calculated to understand the bulking effect of PHN at high retentions;

Bulking efficiency (%) = f(V_{rf}- V,,) / V,,J xlOO (2)

where, Vof is the final oven-dried volume of a specimens and Voi is that of die initial.

2.2. Compression of PHN treated wood

Wood specimens were compressed to 50 % set of radial direction (to the half of the initial thickness) right after impregnation in a specially designed close airtight chamber which is 30 cm long, 17.5 cm wide and 1.0 cm high as internal dimensions. Compression parameters were referred to a previous study conducted by Inoue et al.(1992) to achieve complete fixation of compressive deformation. Accordingly, three series of compression were performed at 171, 180 and 200 °C, considering phase change of BA at elevated temperatures (Smith, 1985; Finch & Gardner; 1970).

Recovery of set (RS) of compressed specimens were determined by boiling test; soaking specimens in water for 30 mm under a reduced pressure and left them in an atmospheric circumstance for a following 210 mm, and then immersing them in boiling water (98 °C) for another 30 mm followed by drying in an oven at 60 °C for 3 days. The radial thickness of oven-dried specimens were measured before and after compression. Five replications were made for each determination and RS was calculated as follows (Inoue et al-, 1992);

$$RS(\%) = (T_r - T_c)/(T_o \cdot T_c) \times 100 \quad (3)$$

where T_r is a specimen thickness after compression and boiling, T_c is me thickness after compression, and To is the initial thickness prior to compression. One hundred % RS indicates a complete recovery at compressive deformation and 0 % represents the perfect fixation.

2.3. Leachability test

To reveal the stability of PHN in wood, weathering was conducted according to the Japanese Industrial Standard (JIS A 9201,1991). Accordingly, PHN-treated - wood was exposed to cyclic leaching in deionized water stirred by a magnetic stirrer (400-500 rpm/mm) at 25 °C for 8 h and to evaporation cycle in an oven at 60 °C for 16 h. The cycles were repeated totally for 10 times. After each leaching period, leachate was sampled to ion chromatography (IC) to analyze boron and phosphorus concentrations. IC (Model 500P of Yokogawa-Hokushin Electric, Japan) was equipped with an ion exclusion column. Analytical conditions were as follows: sample injection: 100 pi; column: SCS5-052+SCS5-252;

temperature: 40 °C; effluent: 1 mM $H:SO_4$ flow rate: 1 mVmm; detector: refractive index detector (Erma, Inc., ERC-751 1). Area of the peaks were converted into ppm concentration values based on the standard lines of the both ions driven from the analysis of standard solutions from 10 to 10.000 ppm to yield une slope of r = 1.000 (±0.001).

2.4. Decay test

A mono culture decay test was conducted according to JIS A-9201 (1991) using a brown-rot fungus, *Tyromyces palustris* (Berk, et Curt) Murr. [FFPRI 0507: Fungal accession number of Forestry and Forest Products Research Institute, Tsukuba, Japan] and a white-rot fungus, *Corwins versicolor* (L. ex Fr.) Quel. [FFPRI 1030], Test blocks were sterilized with gaseous ethylene oxide after measuring their oven-dried weights. Three wood samples of the same treatment were placed in a glass jar which contained medium of *250* g quartz sand + 80 ml nutrient solution with a fully grown fungal mycelia on İt and incubated at 26 °C for 12 weeks. A blank trial was also conducted with the treated specimens at identical conditions of decay test according to the standard, without fungal culture in the glass jars in order to determine the real mass loss in decay test other than caused by chemical leach during test. Nine replicates were tested for each decay fungus. The extent of the fungal attack was expressed as the percentage of mass loss. Uncompressed specimens were subjected to decay test before and after weathering.

3 RESULTS AND DISCUSSION

3.1. Weight gain of wood due to PHN impregnation and bulking efficiency of PHN

Weight gain of wood due to impregnation with PHN is given m Tablfc 1 together with bulking efficiency at different loaâ levels. PHN 130 yielded bener retention levels than PHN 130 G for high concentrations of the treatment solutions. PHN had 13-14 times higher retention in wood man that of saturated solution of BA at ambient temperature (Yalİnkiiiç et al., 1996). This result proved the aforementioned advantage of PHN as enabling required chemical loading into wood (KOHMK, 1996).

Table 1. Weight gain of specimens treaied with PHN 130 and PHN I30G and hulking effect of PHN at different loading levels.

CODE	PHN type	Concentration of aqueous solution	Weight gain % <w/w±5D)"	Bulking efficiency at radial direction %±SD
GA	PH7N130G	10	5 38+0.9	0 16*0.1
NA	PHN 130	10	5.12*1.3	0 11*0 1
GB	PHN130G	50	28.53±S.O	0.35*0.2
NB	PH1N130	50	38.06*10.1	0.07*0.02
GC	PEN 130 G	100	*63.l7t6.5*	0.32±0.2
NC	PHN 130	100	70.02rf.9	010*0.1

' Mean values reflect the weight gain levels of 50 individual specimens. Results were based on the oven dry weight of the wood specimens. SD Standard deviation

In addition, PHN had no remarkable bulking effect on wood cell wall (Table 1), suggesting that no dimension change is expected by PHN impregnation.

3.2. Recovery of sei (RS) of PHN treated-compressed wood

Recovery of set values of compressed wood are given in Table 2. PHN caused 4.0 to 20.3 % recovery after boiling test *of* compressed wood compared to untreated wood. However, this recovery mainly caused by high moisture content (MQ) of wood after treatment. Inoue et al. (1992) found that 17-20 % MC would be optimum for permanent fixation and MC over fiber saturation may have adverse effect on fixation as true for the results given in Table 2. Since, fixation of compressive deformation is closely correlated to applied temperature level during short period compression under press (Inoue et al., 1992), excess moisture can reduce internal heat during the short period of compression that results in stress release differences to avoid permanent fixation

(Dwianto, 1996). Possible water attraction of PHN alike with other water-born boron containing compounds (Yalinkiliç et al., 1995a; Yalinkİliç et al., 1995b; Yalinkiliç et al., 1997c) might also affect the recovery. Therefore, extension of compression time or drying of wood after treatment under fiber saturation point can improve the dimensional stability of compressed-PHN treated wood.

3.3. Boron teachability ~

Stability of PHN in wood at humid conditions was tested along with ten cycles weathering process as described. Boron concentration in the leachates was considered as a base of PHN stability, however, PA was also analyzed as an accompanying fire-retardant ionic compound. As ionic boron appears at sth mm peak at chromatogram, PA ion peak is obtained at $_6$th mm of detection time (Su et al., 1997). Results of the ieachate analysis of wood treated with PHN 130 G at 10 % are given in Table 3.

Table 2 Recovery of set (RS) of compressed PHN-treated wood after boiling test.

Treatment code	RS (9&±SD)'		
	Compressed at 171 C for 15 mm	Compressed at 180 ℃ for 8 mm	Compressed at 200 ℃ for 3 nun
Untreated (20 % MQ	0.0	0.0	0.0
Untreated (saturated)	6.8	4.9	*45*
GA	4.0±0.3	10.9*0.6	8.6*0.1
NA	7.9*0.5	8.3*0.9	15.0*0.6
GB	8.3*1.0	10.8*0.4	10.0*0.6
NB	10.1*0.4	16.3*0.5	15.6*1.0
GC	U.3±0.4	*16.5lÛ.5*	11.1*1.8
NC	13.7*1.6	20 3*0.8	16.8*1.5

* SD: Standard deviation

Table 3 Boron and phosphorous concentration in (he teachates of wood treated with 10% PHN 130 G
(O A coded of treatment series)

Leach, cycle	Boron		and phosphorus		concentration		(ppm)	
	Uncompressed wood				Compressed wood			
			171-C for 15 mm		180 °C for 8 mm		200 "C for 3 mm	
	BA"	Pa"	BA	PA	BA	PA	BA	PA
1	938 3	118 7	847 3	83 6	1018 8	1163	963 6	1145
2	216 8	210	2813	42 3	326 9	240	359 1	460
3	43 0	NDC	871	110	87 5	ND	102 4	ND
4	114	-do-	28 4	N D ,	47 2	-do-	26 8	-do-
5	ND	do-	14 8	-do-	45 0	-do-	248	-do-
6	-do-	-do-	ND	-do-	191	-do-	96	-do-
7	-do-	-do-	do-	-do-	ND	-do-	ND	-do-
8	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
9	-do-	-do-	do-	-do-	-do-	-do-	-do-	-do-
10	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
Total	1209 5	139 7	1258 9	136 9	1544 5	1403	14863	1605

'BA Bone acid,[b] PA Phosphoric acid, °ND Not detectable

Boron and phosphorus leached at earlier cycles of weathering of treated wood similar with the tendency of BA and PA leaching reported earlier (Yalınkılıç et al, 1996, Yalınkılıç et al, 1997b,Su et al, 1997) Compression of treated wood could not support boron and phosphorus fixation at this retention level This result proved the earlier conclusions made on boron fixation that boron would not be protected from leaching by only physical barrier formation in wood against water (Yalınkılıç et al, 1996, Peylo & Wdleitner, 1995) Results of IC analysis of the leachates of *50%* PHN 130 G impregnated wood is given in Table 4

Table 4 Boron and phosphorous concentration in the leachaies of wood treated with 50 % PHN 130 G (GB coded of treatment senes)

Leach cycle	Boron and phosphorus concentration (ppm)							
	Uncompressed wooc				Comoressed wood			
			I71°Cforl5min		180 Cfor 8min		200 Cfcr3min	
	BA'	PA[b]	BA	PA	BA	PA	BA	PA
1	1872 3	314 7	1685 8	2/9 5	1722 9	214 4	1800 3	183 4
2	10921	88 9	9097	1000	842 7	73 1	876 8	80 6
3	4114	69 0	282 8	36 0	284 3	19 5	366 4	20 3
4	136 4	9 2	669	87	129 0	NDC	88 6	ND
5	49 2	ND	"Ï12	ND	29 9	-do-	385	-do-
6	169	-do-	18 8	do-	103	do-	13 1	do-
7	ND	-do-	ND	do-	ND	do-	ND	do-
S	-do-	-do-	-do-	-do-	-do-	do-	-do-	do-
9	-dc-	do-	do-	do-	-do-	do-	-do-	do-
10	-do-	-do	do-	do-	-do-	do-	-do-	do-
Total	3578 3	4818	2995 2	364 2	2734 8	307 0	3183 7	,284 3

・ BA Bone acid [b] PA Phosphoric acid [L] ND Not detectable

Boron somewhat became more stable at initial leaching cycles after compression. Relatively lesser amounts of cumulative leached boron and phosphorus might due from to recrystallization of boron and phosphorus compounds under heating (Smith, 1985; Finch & Gardner, 1970) or aforementioned "ceramic" formation of PHN at elevated temperatures (KOHMIX, 1996). Appearance of a new peak at $_7$»$_3$th mm of detection time at chromatogram of compressed wood at 180 °C can be an indicator of such a conversion. However, disappearance of that peak suggests either that possible new crystals are not so resistant to water leaching for longer time or "ceramic" formation did not take place extensively under applied conditions. Therefore, saturation of treatment solution of PHN had limited contribution to PHN stability in wood. Results of IC analysis of the leachates of undiluted solution treatment of PHN 130 G is given in Table 5. Altheugh total amount of leached boron and phosphorus decreased after compression, both chemicals were still leachable. In other words, compression process, contrary to expectations, had limited delaying effect on leaching rates.

Results of IC analysis of the leachates of wood treated with 10 % PHN 130 is given in Table 6. Recorded leaching tendency was similar with the PHN 130 G treatment at the same concentration level.

Although the leaching ratios decreased by increasing press temperature, boron and phosphorus became more vulnerable to leaching after compression of wood treated with 10 % PHN 130

Compression and saturation of treatment solution to 50 % concentration level had no remarkable improvement on leachability.

Results of IC analysis of the leachates of wood treated wim undiluted solution of PHN 130 is given in Table 8.

Certain reduction was achieved in total amount of boron and phosphorus after compression. Recrystallization of boron and phosphorus or "ceramic" formation of PHN upon dehydration might have caused this reduction. Although ionic boron and phosphorus were still leachable similar to that from uncompressed wood, the considerable difference of cumulative concentrations before and after compression suggests that a certain part of chemical remained in cell wall after weathering. Biological efficiency of PEN treated wood after weathering is, therefore, needed to be known.

3.4. Decay resistance

Results of decay tests of untreated -and treated wood are shown İn Table 9 without preweathering.

Table 5 Boron and phosphorous concentration in nie leachates of wood treated with undiluted PHN 130 G (GC coded of treatment series)

Leach cycle	Boron and phosphorus concentration						(ppm)
	Uncomnressed wood		171^{78}C for15min		Coranressed wood 180 'C for 8mm		200 'C for3min
	BA"	PA-	BA	PA	BA PA	BA	PA
1	2296 7	457 8	1895.1	295 6	2024 4 276 0	1995 0	222.4
2	16341	235.3	1304 9	170.0	1276 8 205.2	1205.7	190.8
3	1063 6	82 6	574.9	27.2	. 5 S 7 J 3 U	633.7	60 0
4	456.2	33 0	147 3	16.0	157 8 9 1	199 1	15 0
5	201.6	110	47 7	ND	519 N D	66.1	ND
6	951	NDC	16 6	-do-	114-do-	28 1	-do-
7	445	-do-	ND	-do-	8 0-do-	14.0	-do-
8	22 7	-do-	-do-	-do-	ND-do-	ND	-do-
9	ND	-do-	-do-	-do-	-do--do-	-do-	-do-
10	-do-	-do-	-do-	-do-	-do- -do-	-do-	-do-
Total	5814.5	819.7	3839 2	508.8	4117 8 5214	4141.7	488.2

"BA: Bone acid,   'PA: Phosphoric acid'ND-Not   detectable

Table 6 Boron and phosphorous concentration in the leachates of wood treated witfi 10% PHN 130 (NA coded of treatment series)

Leach cycle	Boron and phosphorus concentration						(ppm)	
	Uncompressed wood		171 °C forl5min		Compressed wood			
					180 'C for 8mm		200 'C for3mm	
	BA'	PA[b]	BA	PA	BA	PA	BA	PA
1	1100 9	85 8	13321	198 7	1205 1	198 0	1028 4	179 1
2	2313	210	447 0	45 1	339 7	18 1	370 7	319
3	38 0	ND'	810	110	72 2	ND	102 8	ND
4	162	-do-	29 1	ND	308	-do-	25 5	-do-
5	ND	-do-	ND	-do-	99	-do-	94	-do-
6	-do-	-do-	-do-	-do-	ND	-do-	ND	-do-
7	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
8	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
9	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
10	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
Total	1386 4	106 8	1889 2	254 8	1657 7	216 1	1536 8	2110

"BA Bone acid,   '"PA Phosphoric acid, ' ND Not   detectable
Results oflC analysis of the leachates of wood treated with 50% PHN 130 is given m Table 7

Table 7 Boron and phosphorous coocentratian in the leachates of wood treated with 50% PHN 130 G (NB coded of treatment series)

Leach cycle	Boron and phosphorus concentration						(ppm)	
	Uncomoressed wood		171°Cfort5min		Comoressert wood			
					180 'Cfor 8min		200 'C for3min	
	BA*	PA"	BA	PA	BA	PA	BA	PA
1	2003 7	472 5	Not analyzed		1866 3	334 1	1895 0	3191
2	1016 6	69 8	"		873 3	35 1	946 7	70 8
3	166 8	9 0	''		203 5	*m*	294 2	10 0
4	30 7	NDC	''		57 9	*ND*	600	ND
5	10 9	-do-	''		20 4	-do-	210	-do-
6	10 5	-do-	''		110	-do-	93	do-
7	ND	-do-			ND	-do-	ND	do-
8	-do-	-do-	''		-do-	-do-	-do-	-do-
9	-do-	-do-	''		-do-	do-	-do-	-do-
10	-do-	-do-	'.		-do-	-do-	-do-	-do-
Total	3239 2	*5513*			3032 4	382 7	3226 2	399 9

"BA Bone acid, a bPA Phosphoric acid, ' ND Not detectable

Table 8 Boron and phosphorous concentration in the leachaies of wood treated with undiluted PHN 130 {NC coded of treatment series)

Leach cycle	Boron and phosphorus concentration						(ppm)	
	I.lpçofnpres^fid wood		171°Cforl5min		Comnressed wood 180 C for 8min		200 "C for3mm	
	BA"	PA"	BA	PA	BA	PA	BA	PA
1	2524 9	838 7	1883 4	53 10	2057 1	516 2	2087 9	515 0
2	1622 0	277 8	il 536	73 6	1299 5	69 6	1453 0	68 7
3	462 8	120	248 8	9 8	370 3	9 3	553 4	11 0
4	68 0	ND[c]	69 2	ND	94 0	ND	108 5	ND
5	14 8	-do-	22 3	-do-	37 5	-do-	34 5	-do-
6	10 1	-do-	10 0	-do-	12 6	-do-	8 7	-do-
7	ND	-do-	ND	do-	ND	-do-	ND	do-
8	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
9	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
10	-do-	-do-	-do-	-do-	-do-	-do-	-do-	-do-
Total	4702 6	1128 5	3387 3	514 4	38710	595 1	4246 1	594 7

*BA Bone acid. "PA Phosphoric acid, ' ND Not detectable

Table 9 Mass loss of wood treated by PHN types after 12 weeks decay test before weathering

CODE	Mass loss (%±SD	
	Tyromyces palustris	*Coriolus versicolor*
Untreated	*552±40*	49 6±4 5
GA	3 0±0 3	4 2±07
NA	2 9±01	3 1±0 2
G B	18 4±1 3	17 4±1 7
N B	I7 3±18	15 2±1 1
GC	31 0±19	*32 5±I5*
NC	35 2±2 0	30 6±1 5

SD Standard deviation

Most of the recorded mass losses were due to chemical leaching into moisturized quartz sand environment at 12 weeks test duration (Table 10)

Therefore, mass loss caused by fungal attack realized at very low ratios for only lower retention levels of both PHN compounds (Table 11)

Threshold levels of PHN appeared at lower than *5 %* w/w (based on oven dry weight of the wood) against *Tyromyces palustris* and *Coriolus versicolor*. As a consequence, PHN is quite resistant to both decay fungi before weathering and mass loss remained at lower levels than 3 % standard limit of decay resistance But, although migration of PHN into test container can be considered as an advantage of diffusibility of chemical to the wet sites of wood where decay nsk is high, but high migration rate can cause to rapid loss in toxicity against decay fungi by time (Yalınkılıç et a1, 1996) To ascertain the decay resistance of PHN in wet service conditions, specimens after cyclic weathering were exposed to fungal attack Results indicated that 10 % PHN 130 and PHN 130 G treatment had almost no decay resistance after weathering (Table 12) However, remained boron despite cyclic leaching of wood treated with 50 % aqueous or undiluted solutions of PHN 130 G, as expected, performed satisfactory protection against both decay fungi. PHN 130-treated wood was only resistant against *Coriolus versicolor* at these concentrations Tnus, PHN 130 G was more resistant to decay than PHN 130 Supplemental treatments or addition of stabilizing agent to PHN are required for better protection of timber of outdoor use

Table 10.Chemical loss caused by leaching effect of nutrient liquid media during decay test of unleacbed specimens.

CODE	Chemical loss (%, w/w)	Retention of PHN (%wtw)	Remained chemical in wood
GA	1.8	3.6	67.3
NA	1.5	3.6	70.5
GB	21.0	7.5	26.3
NB	23.9	U.J	37.1
GC	38.6	24.5	38.8
NC	38.1	31.9	*45.6*

Table J 1 . Corroded mass toss *leveis* obtained from decay test before weathering,

CODE	Mass loss *(%,* w/w)	
	Tyremycet pmhulru	*Conclus versicolor*
GA	1.2	0.6
NA	1.4	0.0
GB	0.0	0.0
NB	0.0	0.0
GC	0.0	0.0
NC	0,0	0.0

Table 12. Mass toss ofPH7N- treated wood subjected to decay test for 12 weeks after 10 cycles severe weathering.

CODE	Mass loss (%±£D\ w/w)		
	Tyiomyces	*palustris*	*Coriolus versicolor*
GA	29.9*6.2		45.2±l0.9
NA	48.4*12.7		67.3±5.9
GB	3.2*0.8		23.0±1.2
NB	47.5*9.0		8.2±4.3
GC	1.6±0.7		4.6±1.1
NC	33.4±6.3		6.2±1.8

* SD: Standard deviation.

4. CONCLUSIONS

Two* ftBWJy'. developed commercial fire-retardant boron compounds; raW*t3ft*nd. jPHN 130 G were evaluated in terms of boroa leaclaÈffiy mi decay resistance under severe weathering conditions. Results indicated that PHN can be impregnated into wood at required levels of loading and retention level can easily be adjusted by diluting of treatment solution. PHN caused to 4.0 to 20.3 % recovery of compressed set after boiling test. However, this recovery was more Ukely due to high MC of treated wood before compression. Leachability of boron and phosphorus did not differ remarkably by compression of treated wood, although cumulative amounts of leached boron and phosphorus were at lesser concentrations than those leached from uncompressed wood for higher loading levels of PHN. Reduction in total leached amount was attributed to possible recrystallization of boron and phosphorus compounds under elevated temperatures or ceramic" formation property of PHN upon dehydration.

Recorded mass losses of unleached specimens **exposed to** *Tyramyces palustris* **and** *Coriolus versicolor,* representing brown- and white-rot fungi, respectively, indicated that 5 % w/w (based on oven dry weight of wood) PHN can impart complete

100

decay resistance. However, 50 % of impregnated PHN leached out from wood into test container during 12 weeks test duration. Though a slow migration of a compound in wood to the wet sites, where decay risk is generally high, can be favored, excess chemical loss leads loss in protective efficacy by time. To reveal the bioactive performance of remained boron in wood after weathering, leached specimens were subjected to decay test. PHN 130 G treated wood was still remarkably resistant to both decay fungi when it is used over 50 % concentrations. Nevertheless, PHN 130 lost its protective effectiveness and wood became more vulnerable to decay compare to untreated wood after weathering, and only specimens treated with the undiluted solution showed resistance against *Coriolus versicolor.*

In conclusion, PHN can impart total decay resistance to wood at above-ground applications. PHN 130 G type seems more appropriate when using timber in such a service conditions where high decay risk exist. However, supplemental treatment is required to make PHN stable in wood for long term protection at outdoor conditions.

REFERENCES

Arthur, L. T., K. QuilL 1992. Commercial flame retardant applications of boron compounds. In: Flame Retardants '92, Edited by The plastics and Rubber Institute from Pioc. of the Flame Retardants '92 Conferene«. Queen Elizabeth O Conference Centre, Westminster, London, 22-23 Jan., 1992. Else vier Applied Science, London and New York, pp. 223-237.

ASTME84-87. 1988 Standard Test Method for Surface* Burning Characteristics of Building Materials, Test Method E 84-87. American Society for Testing and Materials, Philadelphia, PA, 1988.

Browne, E L 1958. Theories on the combustion of wood and its control. USDA Forest Service, FPL Report 2136.

Browne, F. L, W.K. Tang 1962. Thermogravimetric and differential thermal analysis of wood and of wood treated with inorganic salts during pyrolysis. Fire Research Abstract and Review, National Academy of Science, National Research Council, 4, 76 pp.

Dwianto, W. 1996. Mechanism of permanent fixation of compressive deformation of wood by heat or steam treatment M. Sc. Thesis, Wood Research Institute, Kyoto Univ., Japan, 96 pp.

Ellis, W. D. 1991. Thennogravimetry of wood reacted with hexame thy phosphorus triamide as a flame retardant treatment. *Thermochimica Acta* 188, pp. 213-219.

Finch, A., P.J. Gardner. 1970. Thermochemistry of boron compounds. In: Progress in Boron Chemistry, Vol. 3, Brotnerton, R. J. and Steinberg, H. eds., Pergamon Press, New York, pp. 177-210.

Gerhartz, W. 1985. ed., Fifth Ed., Vol. A4, Weinheim: VCH Publishers, pp. 263-280. Inoue, M., T. Morooka, M Norimoto, R.M. Rowell O. Egawa. 1992. Permanent fixation of compressive deformation of wood D Mechanisms of permanent fixation. FRI Bull., 176, NZ FRI, pp. 181-189.

Inoue, M., N. Kadokawa, J. Nishio, M. Norimoto. 1993. Permanent fixation of compressive deformation by hygro thermal treatment using moisture in wood. *Wood Research and Technical Notes* No. 29, Wood Research Institute, Kyoto Univ., Japan, pp. 54-61

Japanese Industrial Standard (IIS) A 9201. Qualitative standards and testing methods of wood preservatives. 1991.

KOHMTX Co. Ltd. 1996. Creative, Unique, Liquid Ceramics Industry, Kanagawa Prefecture Sagamihara-Shi, Tara 5399-1,229 Japan.

Laks, P. E., R.D. Palardy. 1990. The development of borate-containing flakeboard. Proc. of First Int. Conf. On Wood Protection with Diffusible Preservatives, 28-30 Nov., 1990, Tennessee, USA, pp. 76-79.

LeVan, S. L, H.C. Tran. 1990. The role of boron in flame retardant treatments. Proc. of First Tnt. Conf. On Wood Protection with Diffusible Preservatives, 28-30 Nov., 1990, Tennessee, USA, pp. 39-41.

Lloyd, J.D., D.J. Dickonson, R.J. Murphy . 1990. The probable mechanisms of action of boric acid and borates as wood reservatives. The Int.. Res. Group on Wood Preservation, Document No. IRG/WP/ 1450, 21 pp.

Lloyd, J.D. 1993. The mechanisms of action of boron-containing wood preservatives. Ph.D. Thesis, Imperial College of Science, Technology of Medicine, Department of Biology, *352* pp.

Lyons, J. W. 1970. The Chemistry and Uses of Fire Retardants. Wiley-Interscience Div., John Wiley & Sons, New York, 108 pp.

Nicholas. D. D., L Jin, A.F. Preston. 1990. Immediate research needs for diffusible preservatives. Proc. of First Int.Conf. On Wood Protection with Diffusible Preservatives, 28-30 Nov., 1990, Tennessee, USA, pp. 121-123.

Peyk», A.; Willeimer, H.: The problem of reducing the teachability of boron by water repellents. *HoUorschung* 49, 1995, pp. 211-216.

Smith, R. A. 1985. Boric oxide, boric acid, and borates. In: UDmann's Encyclopedia of Industrial Chemistry, Gerhartz, W. Ed.. Fifth Ed., Vol A4, Weinheim: VCH Publishers, pp. 263-280.

Su, Wen-Yu., MJC Yalinkilic, T. Hata. Y. Imamura, S. Ishihara. 1997. Enhancement of leach and termite resistances of plywood treated with boric compounds. *Mokuzai Gakkaishi* 43(7), pp. 595-601.

Yalinkilic, M.K., E. Baysal. Z. Demirci. 1995a. Effect of boron preservatives on hygroscopicity of Brutia pine wood. *Engineering Science Journal of Pamukkale Univ..* Denizli, Turkey, 1 (2-3), pp. 161-168.

Yalinkilic, M.K., E. Baysal, Z. Demirci 1995b. Effect of boron preservatives on hygrùscopwity of Douglas üre wood. Proc. of First Black Sea Forestry Congress, 22-25, Oct, Trabzon, Turkey, Vol. U, pp. 47-60.

Yalınkılıç, MK-. à Yusuf, T Yoshimura, M Takahashi, KTsunoda lfc>6 Effect of vapor phase formalization of bone acid treated «flood on boron leach ability and bıologıca] resistance Proû frotç Third Pacific Rim Bio-Based Composites Symp » *2 5* Ctec , 1996, Kyoto, Japan, pp *544 55* I

Yalınkılıç, M K , Wen-Yu Su, Z Demirci, E Baysal, M Takahashi, S IshiharaV 1997a Oxygen index levels and analysis of wood treated with metamıne formaldehyde-boron combinations The Int Res Group on Wood Preservation, Document No ffiGIWP 97-30135, 1997, 15 pp

Yalınkılıç. MK. S Yusuf, T Yoshimura, Wen-Yu Su,KTsunoda M Takahashi 1997b Incorporation of phenyl boronic acid treatment with vapor phase formalization The Tnt Res Group on Wood Preservation, Document No IRGIWP 97 40077, 1997, 18 pp

Yalınkılıç, M X , E Baysal, Z Demirci 1997c Water uptake and water repellency of Douglas fir *(Pseudotsuga mennesu* (Mirb) Franco) wood treated with boron compounds Proc of the XI World Forestry Congress, 13-22 Oct , 1997, Antalya, Turkey, Vol 4(E), pp *45*

Yalınkılıç, MK., Ylmamura, M Takahashi, AC Yalınkılıç 1999 In situ polymerization of vinyl monomers during compressive deformation of wood treated with bone acid to delay boron leaching Forest Products Journal, 49(2) 43-51