FIRE RETARDANTS:
Proceedings of
1977 International Symposium
on
Flammability and Fire Retardants

Edited by Vijay Mohan Bhatnagar

# FIRE RETARDANTS: Proceedings of 1977 International Symposium on Flammability and Fire Retardants

May 19–20, 1977 Washington, D.C., U.S.A.

Sponsored by

ALENA ENTERPRISES OF CANADA P.O. Box 1779 Cornwall, Ontario K6H 5V7

> Edited by Vijay Mohan Bhatnagar



a **TECHNOMIC** publication TECHNOMIC Publishing Co., Inc. 265 Post Road West, Westport, CT. 06880

# FIRE RETARDANTS: Proceedings of 1977 International Symposium on Flammability and Fire Retardants

© TECHNOMIC Publishing Co., Inc., 1979 265 Post Road West, Westport, CT 06880

a TECHNOMIC publication

Printed in U.S.A. Library of Congress Card No. 77-90574 ISBN 0-87762-246-9 DEDICATED to

my wife

Alena Sonja Bhatnagar

and children

Indira Devi Bhatnagar Samir Mohan Bhatnagar Sarita Devi Bhatnagar Monika Devi Bhatnagar

Love is indeed an ecstasy when it is continuous

After all there is but one race - humanity

---- George Moore

(1852-1933)

#### Symposium Chairman

Vijay Mohan Bhatnagar Alena Enterprises of Canada P.O. Box 1779 Cornwall, Ontario K6H 5V7, Canada

## Polymers and Plastics Session — Chairman

Gert F. Baumann Mobay Chemical Corp. Pittsburgh, Pennsylvania 15205, U.S.A.

# Textiles, Fibers, and Fabrics Session - Chairman

Stephen B. Sello J. P. Stevens and Co. Inc. Garfield, New Jersey 07026, U.S.A.

# Coatings and Testing Session — Chairman

Sven Hadvig Technical University DK-2800 Lyngby, Denmark

#### Luncheon Speakers

Vladimir Mischutin White Chemical Corp. Bayonne, New Jersey 07002, U.S.A.

Clayton Huggett National Bureau of Standards Washington, D.C. 20234, U.S.A.

#### **PREFACE**

In recent studies, it has been shown that the fire retardant industry is keeping a good growth record. The growth of this market can be expected to grow by 15.5% per year through the next ten years. In 1975, the market for flame retardant chemicals was in the range of 312 million pounds to 360 million pounds. It is expected to reach 425 million to 525 million pounds by 1980. Phosphate plasticizer sales were about 90 million pounds in 1976. 40–60% urethanes were flame retarded in 1976. The forecast is for 6–10% per year growth for the next five years. In 1976, 6–8% polystyrene was fire retarded as compared to 4–5% ABS, 10–15% unsaturated polyesters, 15–20% epoxy, less than 1% polyolefins, and 20% PVC. Another study revealed that the consumption of fire retardant chemicals in plastics will be 787 million pounds in 1980 as compared to about 383 million pounds in 1975. The same report states that the control of smoke and toxic gases from burning materials in an important area of interest in fire retardant technology. A summary consumption of smoke suppressant chemicals during 1975–1985 is given as follows:—

Total lbs. 189 million lbs. in 1975 621 million lbs. in 1980 1,070 billion lbs. in 1985

i.e. an average annual growth during 1975-85 of 18.9%.

With these hopeful and encouraging figures, surely new ways will be found of evolving plastics and other materials with new and better fire retardant and less smoke properties. More research and development work, for applications in several markets especially furniture, construction, furnishings, bedding, carpets, textiles, transportation, etc., will not only increase the demand of flame retardant products but will also keep the future of this fast growing industry as bright as many industries dream of.

209 Dover Road Cornwall, Ontario K6H 5V7, Canada Vijay Mohan Bhatnagar Symposium Chairman

#### **CONTRIBUTORS**

#### Polymers and Plastics Session .1.

- 1. Barlow, J. W. and Schraufnagel, R. A., Department of Chemical Engineering, University of Texas, Austin, Texas 78712.
- 2. Barron, S., Department of Chemistry, State University College, Buffalo, New York 14222.
- 3. Brady, D. G., Moberly, C. W., Norell, J. R. and Walters, H. C., Phillips Petroleum Co., Bartlesville, Oklahoma 74004.
- 4. Curtat, M. and Vinuales, G., Société Nationale des Poudres et Explosifs, Centre de Recherches du Bouchet, 91710 Vert-le-Petit, France.
- 5. Green, J., Cities Service Co., Cranbury, New Jersey 08512.
- 6. Hamilton, J. P. and Weibel, A. T., FMC Corp., Princeton, New Jersey 08540.
- 7. Lecolier, S., Le Roy, P. and Quivot, M., Société Nationale des Poudres et Explosifs, Centre de Recherches du Bouchet, 91710 Vert-le-Petit, France.

#### Textiles and Fabrics Session

- 8. Lepchenske, J., Central States Diversified Inc., 5221 Natural Bridge, St. Louis, Missouri 63115.
- 9. Schoppee, M. M., Skelton, J. and Abbott, N. J., Fabric Research Laboratories, Route 128 at U.S. 1, Dedham, Massachusetts 02026.
- 10. Wolf, R., Sandoz AG, Dyes Department—Applications, CH-4002 Basle, Switzerland.

### Coatings and Testing Session

- 11. Bryan, J. L., Fire Protection Curriculum, College of Engineering, University of Maryland, College Park, Maryland 20742.
- 12. Leiner, L. H., Kifer, E. W. and Regent, D. M., Koppers Co. Inc., Monroeville, Pennsylvania 15146.
- 13. Megal, C. A., Grand, A. F. and Sabala, J. F., Velsicol Chemical Corp., Technical Center, 1975 Green Road, Ann Arbor, Michigan 48105.
- 14. Neal, J. E. and Neisel, R. H., Johns-Manville Sales Corp., Ken-Caryl Ranch, Denver, Colorado 80217.
- 15. Parker, J. A., Kourtides, D. A. and Stocks, R., Ames Research Center, N.A.S.A., Moffett Field, California 94035.
- 16. Redfern, J. P., Stanton Redcroft, Copper Mill Lane, London SW17 OBN, England.

### Polymers and Plastics Session .2.

- 17. Lum, R. M., Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974.
- 18. Monte, S. J., Sugerman, G. and Seeman, D. J., Kenrich Petrochemicals Inc., Foot of East 22nd Street, Bayonne, New Jersey 07002.
- 19. Quinn, E. J. and Dieck, R. L., Research and Development Center, Armstrong Cork Co., Lancaster, Pennsylvania 17604.
- Takahashi, A., Research Center—Maruzen Oil Co. Ltd., Tokyo, Japan and Shimizu, M., Maruzen Oil of U.S.A. Inc., 641 Lexington Avenue, New York, New York 10022.
- 21. Williams, J. B., Nelson, G. L., O'Connell, W. J. J. and Bridgman, A. L., General Electric Co., Lexan Lane, Mount Vernon, Indiana 47620.

# CONTENTS

Contributors
POLYMERS AND PLASTICS Session .1.
Flame Spread Rates over Polyurethane Foams. J. W. Barlow and R. A. Schraufnagel 1
An Investigation of the Effects of High Temperatures Upon Selected Industrial Polymeric Materials. S. Barron
Intumescence: A Novel Effective Approach to Flame Retarding Polypropylene. D. G. Brady, C. W. Moberly, J. R. Norell and H. C. Walters
Application of an Expression of the Regression Rate to the Determination of Combustibility. M. Curtat and G. Vinuales
Flame Retarding Polyolefins. J. Green
Synthetic Triaryl Phosphates vs Cresylic Esters as Flame Retardants. J. P. Hamilton and A. T. Weibel
Application of Ternary Synergistic Systems of Fire-Retardants to Improve Flame Retardancy in Rigid Polyurethane Foams. S. Lecolier, P. Le Roy and M. Quivot 54
TEXTILES, FIBERS, AND FABRICS Session
The Transient Thermo-Mechanical Response of Protective Fabrics to Radiant Heat.  M. M. Schoppee, J. Skelton and N. J. Abbott
FLAM-A-GARD Fire Resistant Kraft Papers. J. Lepchenske
Flame Retardant Dope Additives for Regenerated Cellulose Fibers. R. Wolf 91
COATINGS AND TESTING Session
Project People — A Study of Human Response in Fire Incidents. J. L. Bryan 103
Fire Retardants in Wood. L. H. Leiner, E. W. Kifer and D. M. Regent
A Comparison of Laboratory Scale Smoke Test Methods. C. A. Megal, A. F. Grand and J. F. Sabala
Fire Protection of Steel. J. E. Neal and R. H. Neisel
Flammability Characteristics of Some Thermoplastic Polymers. J. A. Parker, D. A. Kourtides and R. Stocks

The Measurement of the Oxygen Index at Elevated Temperatures and Its Application to the Study of Plastics. J. P. Redfern
Laser-Pyrolysis of MoO <sub>3</sub> and MoO <sub>3</sub> /PVC Systems. R. M. Lum
Flame Retardance with Titanium Coupling Agents. S. J. Monte, G. Sugerman and D. J. Seeman
Polyaryloxyphosphazenes — A New Class of FR, Low-Smoke Polymers. E. J. Quinn and R. L. Dieck
Brominated Poly-Para-Vinyl Phenol Fire Retardants Reacting with Other Polymers.  A. Takahashi and M. Shimizu
Lexan 940 <sup>®</sup> — A Uniquely Fire-Retarded Polycarbonate. J. B. Williams, G. L. Nelson, W. J. J. O'Connell and A. L. Bridgman

.

#### FLAME SPREAD RATES OVER POLYURETHANE FOAMS

J. W. Barlow and R. A. Schraufnagel

Department of Chemical Engineering The University of Texas at Austin Austin, Texas 78712

#### **PREFACE**

Reported herein is a summary of our initial findings regarding the mechanisms controlling the rate of flame spreading through rigid polyurethane foams. This work was sponsored by the National Science Foundation through Grant No. GK42148. Further details of some aspects of this work may be seen in Mr. R. A. Schraufnagel's Ph.D. thesis to issue in late 1977.

Many people within the Department of Chemical Engineering of the University of Texas at Austin were instrumental to the technical success of this project. Their support is gratefully acknowledged as is that provided by the Plastics Institute of America in the form of a fellowship to Mr. R. A. Schraufnagel.

#### **ABSTRACT**

A newly developed, tiltable, wind tunnel is described in which polymer foam samples can be burned under well defined conditions. As the sample and tunnel are rotated from horizontal to vertical positions, the rates of forward burning flame spread over non-retarded foams are observed to increase approximately two orders of magnitude. The observed changes in flame spread rate are well correlated with changes in the rate of radiant energy fed back from the flame to the polymer surface, as calculated from measurements of the flame length, temperature, and angle made with respect to the polymer surface. Steady state burning rates are observed for all test conditions and the foam samples tested appear to burn as thermally thin materials.

#### INTRODUCTION

Over the years, numerous flammability tests have been developed to assess the potential fire hazard of polymeric materials. Unfortunately, the flammability behavior of a material has been often observed to be closely related to the type of test employed with the result that no single test has been found which can be trusted to correlate or predict the material flammability behavior in a large scale conflagration.

This work was undertaken for the purpose of investigating the effect of testing conditions on the rate of flame spreading over polyurethane foams. The objectives of this activity were (1) to observe the magnitude change in flame spread rates possible when testing conditions are changed

and (2) to identify the predominant mechanisms controlling the rate of flame spread and to relate these mechanisms to testing conditions and material properties, and (3) to consider ways by which small scale flame spread testing could be used to estimate larger scale flame spreading under similar conditions.

This paper primarily describes experimental and theoretical activities involved toward accomplishing the first two objectives above. Flame spread rates over non-flame retarded polyurethane foams were measured in a newly developed convection tunnel testing device. Flame spread rates could be caused to vary over two decades depending on the test conditions used. The major experimental parameters controlling the rate of flame spread were found to be test specimen geometry and orientation with respect to the flame, convective gas velocity and direction with respect to the flame and the thermophysical properties of the polymeric material. The observed flame spread rates in the direction of forced convection were successfully correlated with test conditions by considering their effect on the intensity of radiant heat transfer from the flame to the polymer substrate.

#### A MODEL OF FLAME SPREAD BY RADIANT HEATING

The very similar theories put forth by deRis [2, 3] postulate that the processes controlling flame spread occur in an ignition region,  $\delta$ , at the leading edge of the flame adjacent to the fuel surface. In this region, the fuel is heated by flux, q, from the ambient temperature,  $T_o$ , to the ignition,  $T_{ig}$ , and the time required to do this is inversely proportional to the rate of advance of the flame edge, V, commonly called the flame spread rate. Their solutions to the combined solid and gas phase energy conservation equations lead to the following simplified equations:

Thin fuel bed case ( $\tau < 1$ )

$$V \cong \frac{q\delta}{pCt (T_{ig} - T_o)}$$
 (1)

Thick fuel bed case ( $\tau > 1$ )

$$V \cong \frac{q^2 \delta (1.272)}{pCK (T_{ig} - T_o)^2}$$
 (2)

where p, C, K, and t are the solid fuel density, specific heat, thermal conductivity, and thickness, respectively, and  $\tau$  is a non-dimensional critical thickness parameter, computed by the expression

$$\tau = t \left( pCV/K\delta \right)^{1/2} \tag{3}$$

which represents the extent to which subsurface thermal gradients are important to the heating process of the fuel from  $T_o$  to  $T_{ia}$ .

With reference to Figure 1, from Pagni [4], there are several possible energy flux terms which could help to preheat the polymer fuel. Of these terms, solid phase internal convection,  $q_{ci}$ , is not likely to be important due to the closed nature of the foam cells, solid state thermal conductivity is so low that  $q_{Kg}$  is probably unimportant, and radiation transfer by an "ember burning" process common in cellulose combustion does not occur in polyurethanes [5]. The surface convection flux,  $q_{cs}$ , is unimportant for flames propagating into the wind and may be relatively unimportant for forward propagation if the relative velocity of the flame and the wind is about zero. The turbulent convection term,  $q_{ct}$ , caused by convective preheat flux from hot gases in the flame plume to the unburned fuel is effectively independent of the propagation rate, to a first approximation [6].

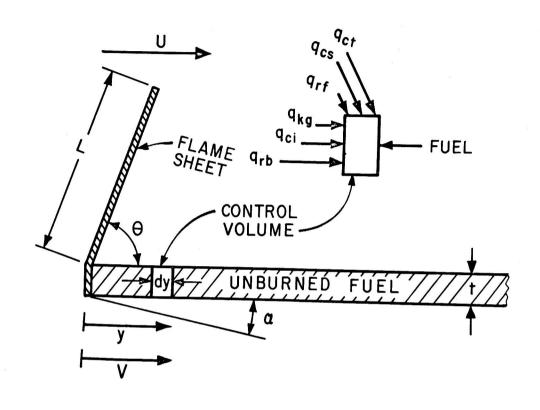


Figure 1. A model of the flame spread process.

Radiant flux from the flame,  $q_{rF}$ , is likely to be the term which changes dramatically when the flame angle,  $\theta$ , is varied either by changing the angular position of the sample,  $\alpha$ , or the wind speed, U. The flux term is, also, likely to be higher than that observed in cellulose fires because of the higher emissivity resulting from higher concentrations of soot in polymer flames [7, 8]. For these reasons, only radiant energy feedback from the flame is considered to be important to this discussion.

By considering the flame to be a planar, opaque, radiating body, the net rate of radiant energy transfer from the flame surface, "1", to the polymer surface, "2", can be written as

$$Q_{12} = A_1 F_{12} \epsilon_1 \sigma T_1^4 = A_2 F_{21} \epsilon_1 \sigma T_1^4 = \dot{Q}_f(LW) F_{12}$$
(4)

where  $A_1$  is the planar area of the flame equal to the product of flame length, L, and width, W.  $A_2$  is the area of the polymer surface equal to the product of polymer length, Y, and width, W.  $\epsilon_1 \sigma T_1^{-4}$  is the flux  $\check{O}_f$  radiating from the grey body flame with uniform temperature  $T_1$  much greater than the polymer surface temperature  $T_2$ .  $F_{12}$  is the geometric view factor between the two intersecting planes as determined by Sparrow [9].

Figure 2 shows the typical view factor relationship computed specifically for the case of flames with dimensionless lengths X = L/W inclined at various flame angles  $\theta$  toward a polymer surface of dimensionless length Y = y/W = 3.0. Here it can be seen that the fraction of flame radiant energy received by the polymer surface is a strong function of the angle  $\theta$ , decreasing from 1.0 at  $\theta = 0^{\circ}$  to 0 at  $\theta = 180^{\circ}$ . The fraction received is also a function of the ratio of flame length to polymer length, approaching an asymptotic upper limit as X/Y approaches zero.

The distribution of radiant energy received by the polymer surface is not constant over that surface. Rather the radiation intensity is highest near the point of intersection of the two planes and decreases toward zero as the ratio of the distance from the point of intersection along the polymer surface to the flame length becomes very large. The flame propagation models, summarized in Equations (1-3), require knowledge of the preheat length,  $\delta$ , and the average intensity of absorbed radiation, q, in this length. One way to define the zone,  $\delta$ , is to determine the distribution of radiation on the polymer surface as a function of distance from the intersection of the two planes. The distribution can be easily found by differentiating the view factor expression,  $F_{1,2}(W, Y, L, \theta)$ , with respect to distance y. That is, the flux received by area element,  $W\Delta y$ , located a distance y from the intersection is just

$$\dot{Q} = \frac{\dot{Q}_{F}(LW) \left[F_{12}(y + \Delta y) - F_{12}(y)\right]}{W\Delta y}$$

and

$$\dot{Q}_{s}(Y) = \lim \dot{Q} = \dot{Q}_{F} L \frac{\partial F_{12}}{\partial y}$$

$$\Delta v \to 0$$
(5)

where  $\dot{\mathbf{Q}}_{\mathsf{F}}$  is  $\epsilon_1 \sigma \mathsf{T}_1^4$ , the flux emitted from the flame.

Figure 3 shows a typical plot of reduced flux distribution obtained by numerically differentiating the view factor, arbitrarily computed for a flame length of 8 inches. Here it is seen that when  $\theta$  is small,  $\dot{Q}_s(y)$  is essentially constant for y less than L but drops sharply when y exceeds L. Insofar as these distributions are reasonably square, it seems reasonable to assign a square distribution such that  $<\!Q_s>$  is constant for y less than  $\delta$  and zero for y greater than  $\delta$ . A total radiation balance of the polymer surface then yields

$$\langle \dot{Q}_s \rangle \delta W = \beta W \int_0^\infty \dot{Q}_s(y) dy = \beta \dot{Q}_f LW F_{12}^*$$
 (6)

where  $\beta$  is the major fraction of radiation falling on the preheat zone and  $F_{12}^* = F_{12}(W, \infty, L, \theta)$  is the asymptotic value of the view factor for an "infinite" length polymer surface, a number between zero and one. One can likewise write

$$<\dot{Q}_s K \delta W = W \int_0^{\delta} \dot{Q}_s(y) dy = W \dot{Q}_f L F_{12} (W, \delta, L, \theta)$$

so that the zone length  $\delta$  is that value of y such that

$$F_{12}(W, \delta, L, \theta) = \beta F_{12}^* = F_{12}(\delta)$$
 (7)

The entire problem of specifying the flux on the preheat zone and the preheat length thus reduces to establishing  $\beta$ , the fraction of the asymptotic view factor. With reference to Figure 3,

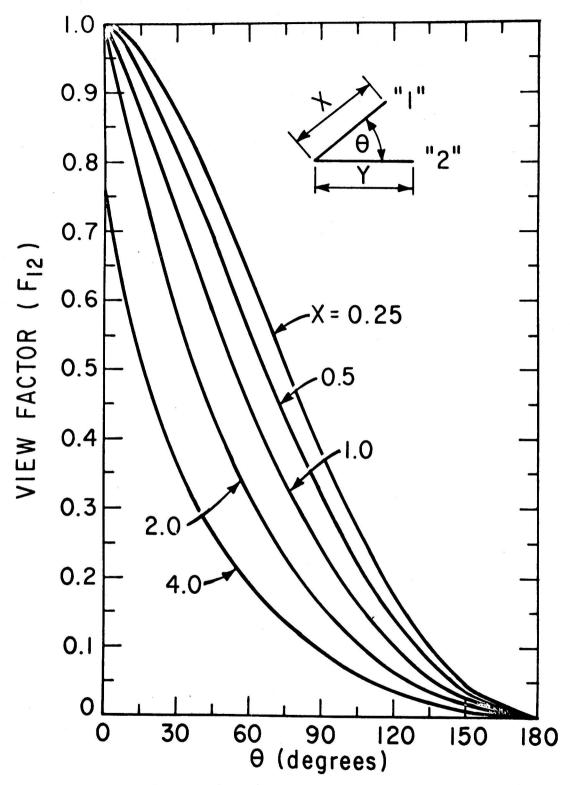


Figure 2. View factors, calculated for various dimensionless flame lengths and angles, for radiant interchange with dimensionless polymer surface, Y = 3.0.

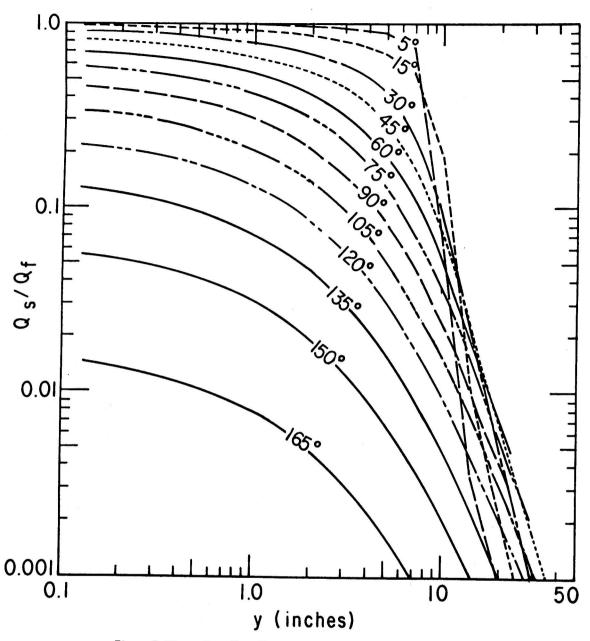


Figure 3. The radiant flux distribution along the polymer surface for various flame angles and a flame length of 8.0 inches.

 $\beta\cong 1.0$  and  $\delta\cong L$  at low flame angles. At large angles, the distributions are less square and the choice of  $\beta$  is somewhat obscure.

Table 1 shows values of  $\delta$  computed for  $\beta$  = 0.90 and various flame lengths and angles. As will be shown later,  $\beta$  = .90 is a reasonable value insofar as the resulting zone lengths are well correlated with observed values. It suffices to note here that the preheat length is a strong function of both flame length and intersection angle. Once  $\delta$  is specified, the flux absorbed by the polymer surface with absorptivity,  $a_2$ , in the preheat region, q, is found from Equation (6) to be

Table 1. Evaluation of  $\delta$  for 90% of Asymptotic Integral View Factor

Œ														
Degrees	.0	ိုက	10	15°	30 0	45 °	09	75	06	105	120	135	150	165
Flame Length, inches						-	6,	ô, Inches			,			
ı.	.45	.47	.50	.55	.80	.92	1.12	1.35	1.50	1.70	1.85	1.85	1.95	2.00
1.0	06.	.95	.975	1.13	1.40	1.71	1.97	2.35	2.50	2.65	2.65	2.80	2.80	2.86
1.5	1.35	1.43	1.47	1.60	1.95	2.45	2.80	3.00	3.35	3.50	3.60	3.65	3.70	3.67
2.0	1.80	1.89	1.93	2.12	2.65	2.95	3.37	3.75	3.95	4.00	4.25	4.45	4.15	4.43
3.0	2.70	2.82	2.92	3.00	3.63	4.12	4.75	5.00	5.40	2.60	5.80	5.80	5.70	5.65
4.0	3.60	3.73	3.85	4.00	4.82	5.35	5.80	9.00	6.30	6.75	6.75	9.90	6.80	6.87
5.0	4.50	4.95	5.15	5.35	5.67	6.20	6.85	7.30	7.50	7.70	7.80	7.80	7.80	7.56
6.0	5.40	5.60	5.71	5.84	6.65	7.30	7.80	8.10	8.75	8.90	9.10	8.80	3.60	8.60
7.0	6.30	6.65	6.80	6.95	7.47	8.20	9.05	9.60	10.50	10.25	10.05	9.50	9.50	9.44
8.0	7.20	7.35	7.57	7.70	8.50	9.45	10.10	10.65	11.50	10.75	10.80	10.50	10.50	10.15
9.0	8.10	8.48	8.72	8.95	6.67	10.50	11.00	11.35	11.50	11.50	11.50	11.60	11.50	10.67
10.0	9.00	10.00	9.95	10.05	10.50	11.20	11.75	12.00	12.00	12.00	12.00	12.00	12.00	10.78