Connecting People, Science and Regulation

THE MECHANISM OF POLYMER MIGRATION
A DESCRIPTIVE APPROACH

PDA WORKSHOP
EXTRACTABLES – LEACHABLES
Brussels
13-14 March, 2014

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THE PHYSICS OF POLYMER LEACHING

GENERAL FORMULA FOR DESCRIPTION OF POLYMER MIGRATION:

$$\frac{m_{F,t}}{A} = 0.1\, c_{p,o}\, \rho_P\, d_P \left(\frac{\alpha}{\alpha+1}\right)\left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^{\,2}} \exp\left(-D_P\, t\, \frac{q_n^{\,2}}{d_P^{\,2}}\right)\right]$$

LEACHING WILL DEPEND UPON:

1. **SOLUBILITY** OF LEACHABLE IN POLYMER

2. **DIFFUSION** OF LEACHABLE TRU POLYMER

1. SOLUBILITY OF LEACHABLE IN POLYMER

IS IMPACTED BY

A. POLYMER MORPHOLOGY (Semi-Crystalline vs. Amorphous)

B. TEMPERATURE

C. AGEING – STERILIZATION

D. STRUCTURE & MOLECULAR WEIGHT OF LEACHABLE

1. SOLUBILITY OF LEACHABLE IN POLYMER

A. POLYMER MORPHOLOGY

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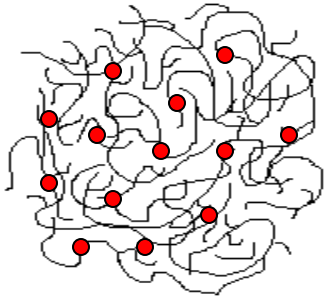
A. POLYMER MORPHOLOGY

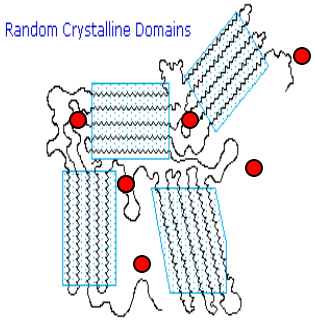
POLYMER C/C SYSTEMS:

= EITHER **AMORPHOUS** OR **SEMI-CRYSTALLINE**

AMORPHOUS

PC, PVC, PS, PU





SEMI-CRYSTALLINE:

PE, PP, PET, EVA

PEEK, Nylon

•: POLYMER ADDITIVE/IMPURITY

DISSOLVES IN AMORPHOUS PHASE

INSOLUBLE IN CRYSTALLINE PHASE

CRYSTALLINE SITES: BARRIER FOR MIGRATION

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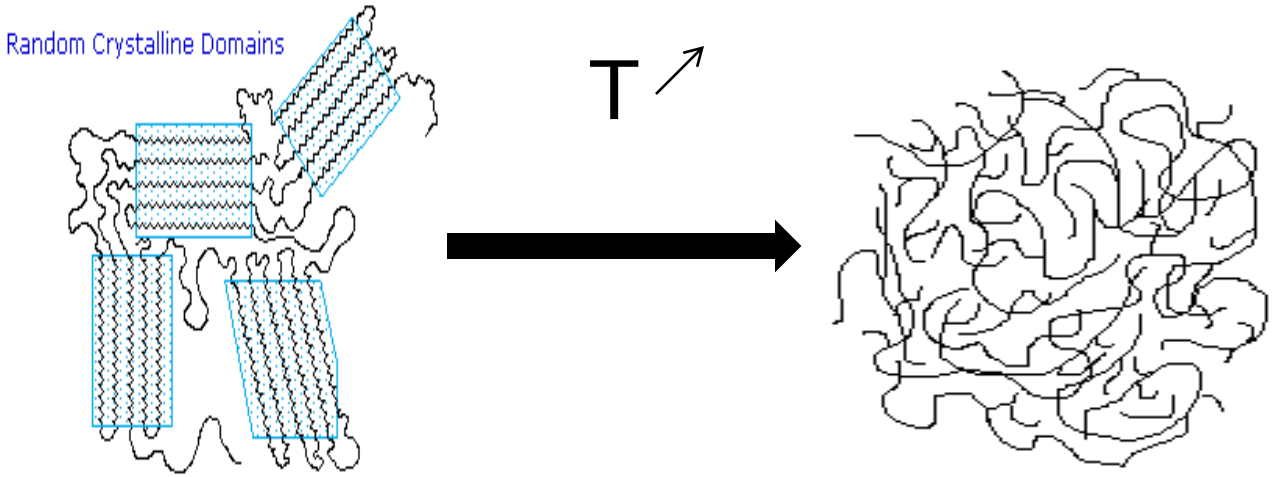
T ↑ ➔ SOLUBILITY ↑



Room temperature

Melt Temperature

RESULT: BETTER SOLUBILITY at higher T

LESS “CRYSTAL BARRIER” FOR MIGRATION

1. SOLUBILITY OF LEACHABLE IN POLYMER

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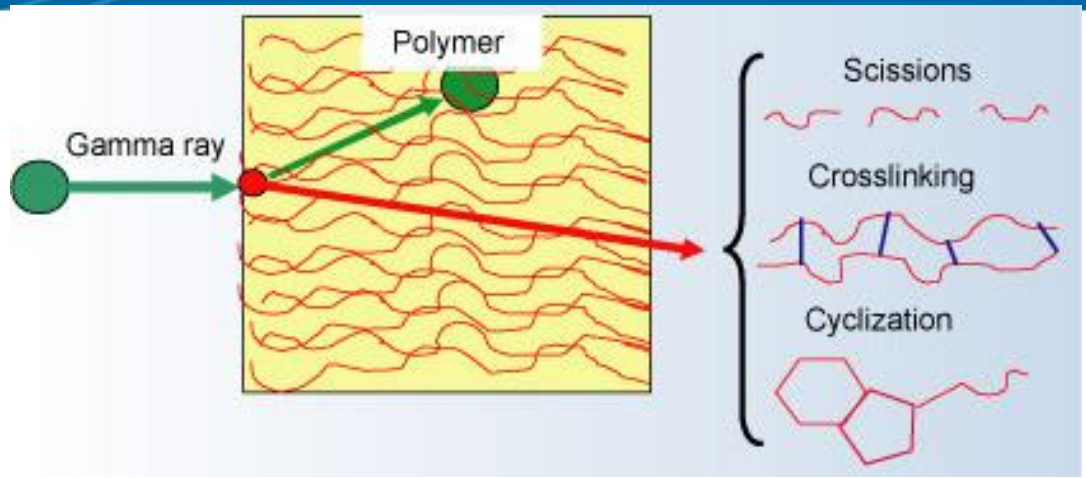
C. AGEING - STERILIZATION



POLYMER DEGRADATION (e.g. Scissions, Crosslinking, cyclization)

POLYMER ADDITIVE DEGRADATION

CHANGES IN POLYMER CRYSTALLINITY

This will impact the: LEACHABLES SOLUBILITY

LEACHABLES MIGRATION

CONCLUSION: TEST FOR EXTRACTABLES AND LEACHABLES ON STERILIZED C/C SYSTEMS

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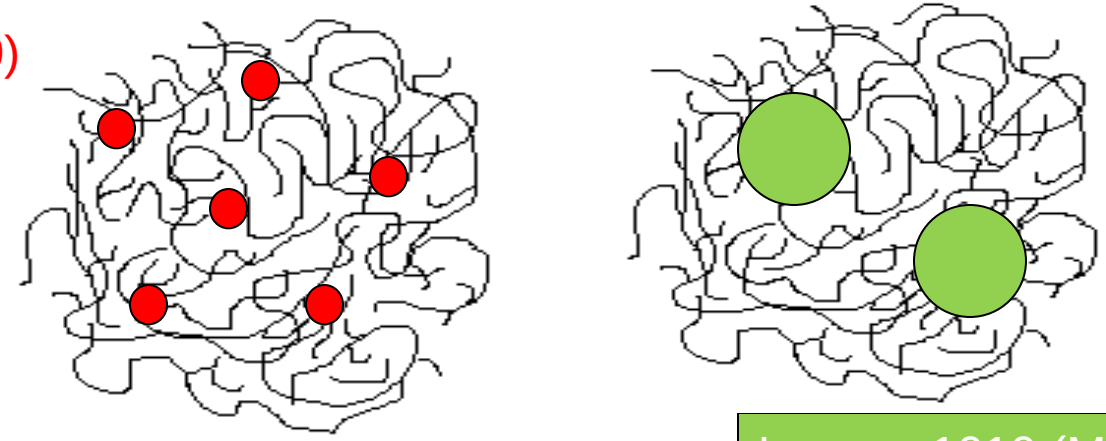
D. STRUCTURE & MOLECULAR WEIGHT

MOLECULAR WEIGHT: Larger Molecules – Lower solubility

BHT (MW 220)



Irganox 1010 (MW 1176)

MELTING POINT: higher T_{melt} - lower solubility

T_{melt} impacted by: - molecular symmetry
- crystallinity

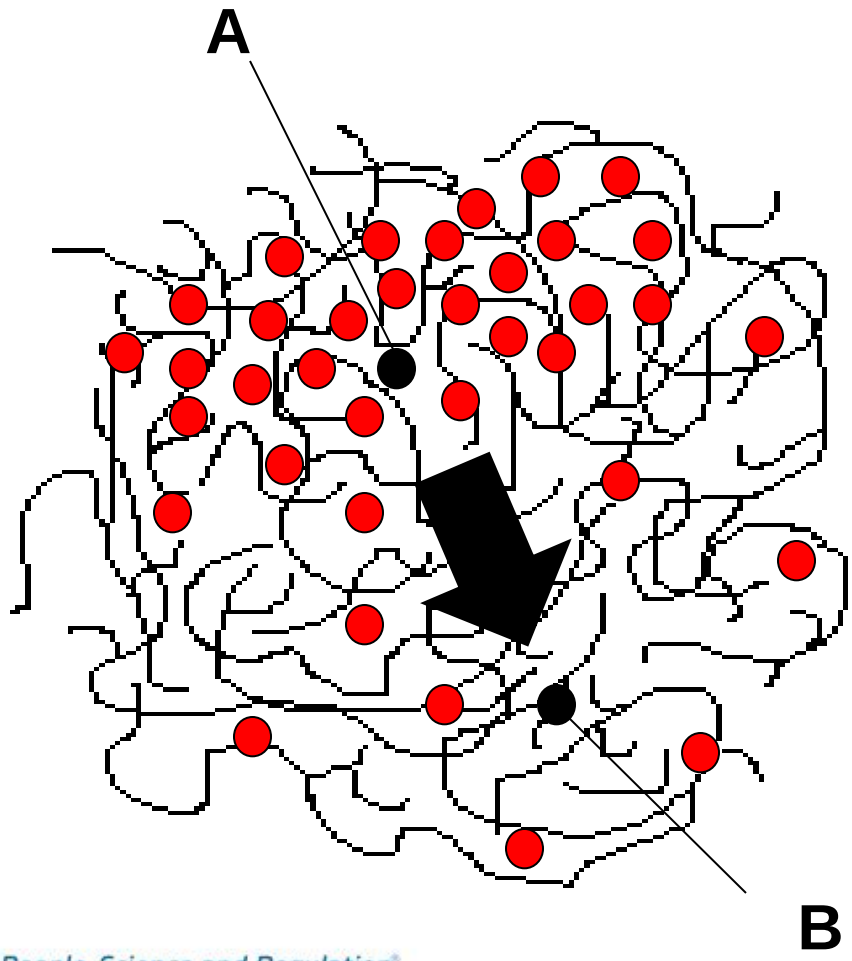
POLARITY "MATCH": "Alike dissolves alike"

LEACHING WILL DEPEND UPON:

1. **SOLUBILITY** OF LEACHABLE IN POLYMER

2. **DIFFUSION** OF LEACHABLE TROUGH POLYMER

2. DIFFUSION OF LEACHABLES THROUGH POLYMERS



FICK's LAW

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2}$$

With D = Diffusion coefficient

$$D = D_0 \exp(-E/RT)$$

2. DIFFUSION OF LEACHABLES THROUGH POLYMERS

IS IMPACTED BY

A. POLYMER MORPHOLOGY

B. TEMPERATURE

C. POLYMER TYPE (T_g)

D. LEACHABLES MOLECULAR WEIGHT (MW)

E. CONTACT FLUID

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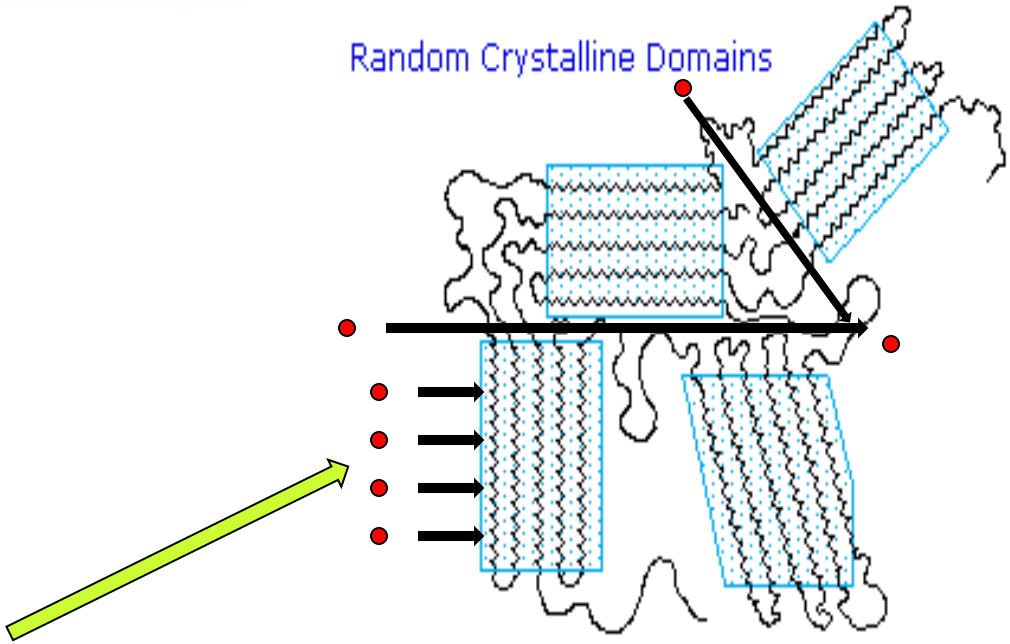

CRYSTALLINE SITES: IMPERMEABLE BARRIER FOR POLYMER ADDITIVES

➔ LOWER DIFFUSION IN SEMI-CRYSTALLINE POLYMERS (for low T_g materials)

FILLER PARTICLES: ADD. DIFFUSION BARRIER

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B. TEMPERATURE

$$D = D_0 \exp(-E/RT)$$

OR, IF $T \uparrow \rightarrow D \uparrow$

Diffusion of impurities/polymer additives will increase exponentially with an increasing temperature

Or, the higher the temperature, the faster the diffusion!

2. DIFFUSION OF LEACHABLES THROUGH POLYMERS

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C. POLYMER TYPE

GLASS TRANSITION TEMPERATURE (T_g)

DEFINITION: Temperature when a polymer goes from a "glassy" state (< T_g) to a "rubber" state (> T_g)

EXAMPLES	
LDPE	T_g = -125°C
POM	T_g = -50°C
PP	T_g = -25°C
PBT	T_g = +70°C
PVC	T_g = +81°C (non plasticized)
ABS	T_g = +110°C
PC	T_g = +150°C

DIFFUSION IN APOLAR > DIFFUSION POLAR POLYMERS

C. POLYMER TYPE

FREE VOLUME

DEFINITION: ratio of the interstitial space between molecules to the volume of the polymer

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Polymers in rubbery state ($T_g < T_{room}$): typically higher free volume

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Promotes diffusion!!

C. POLYMER TYPE

EXAMPLE FOR COC *(Cyclic Olefin Copolymer)*

- T_g ranges from 70-130°C (depending on grade)
- AMORPHOUS polymer

O_2 diffusion : O_2 (small molecule) can diffuse through interstitial space (free volume of the COC)

H_2O diffusion : H_2O (larger polar molecule) will not diffuse through interstitial space of a non-polar polymer

General diffusion : **diffusion of larger organic compounds will be low** because of low availability of interstitial space (low free volume) in glassy COC polymer

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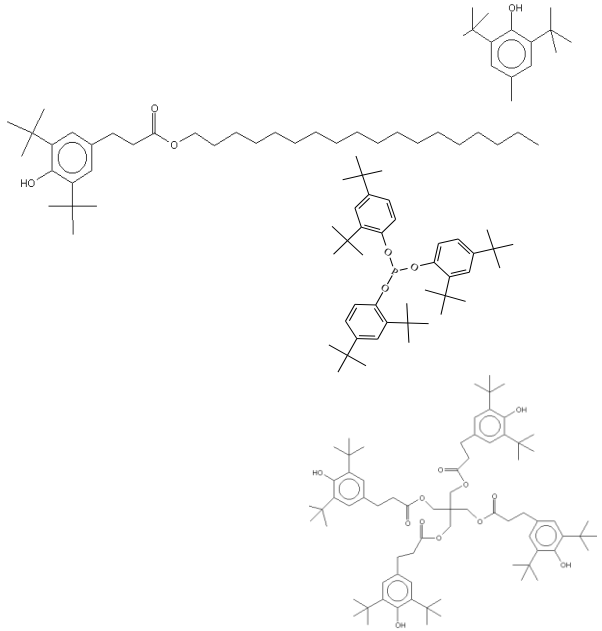
D. LEACHABLES MOLECULAR WEIGHT

OLIGOMERIC ADDITIVES → REDUCING DIFFUSION



BHT: M.W. 220: HIGH DIFFUSION

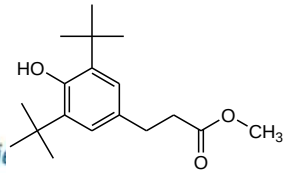
Irganox 1076: M.W. 530

Irgafos 168: M.W. 646

Irganox 1010: M.W. 1176: LOW DIFFUSION

P.A. DEGRADATION INTO SMALLER MOLECULES → FASTER DIFFUSION OF DEGRADANTS

Example:



3,5-Di-*tert*-butyl-4-hydroxyphenyl propionic acid methyl ester

Degradation product of Irganox 1010 /Irganox 1076

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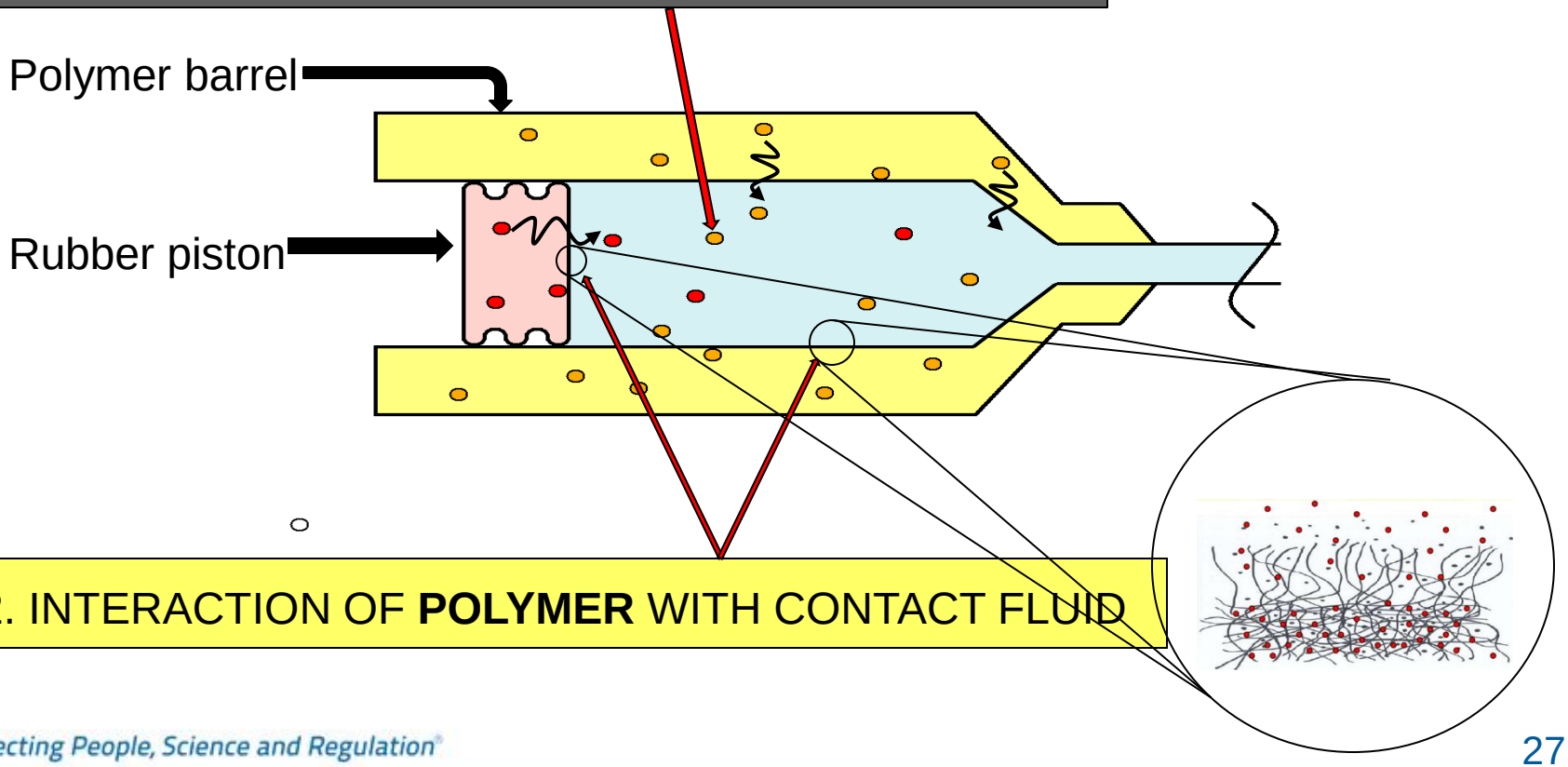
E. CONTACT FLUID

E. CONTACT FLUID

2 IMPORTANT ASPECTS:

1. SOLUBILITY OF **LEACHABLE** IN CONTACT FLUID



2. INTERACTION OF **POLYMER** WITH CONTACT FLUID

E. CONTACT FLUID

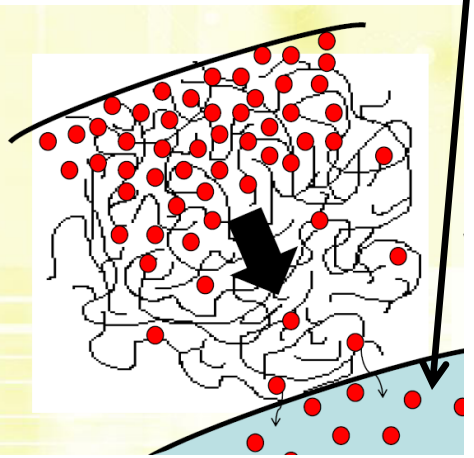
1. INTERACTION CONTACT FLUID - LEACHABLE

IN GENERAL:

ORGANIC/HYDROPHOBIC CONTACT FLUIDS = HIGH SOLUBILITY SOLVENTS

WFI/HYDROPHILIC CONTACT FLUIDS = LOW SOLUBILITY SOLVENTS

E. CONTACT FLUID



EFFECTIVE DISSOLUTION OF LEACHABLE AT POLYMER SURFACE

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EFFICIENT SURFACE LOSS MECHANISM

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LEACHING IS DIFFUSION CONTROLLED

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LEACHING IS PROPORTIONAL TO $t^{1/2}$

E. CONTACT FLUID

2. INTERACTION CONTACT FLUID – POLYMER

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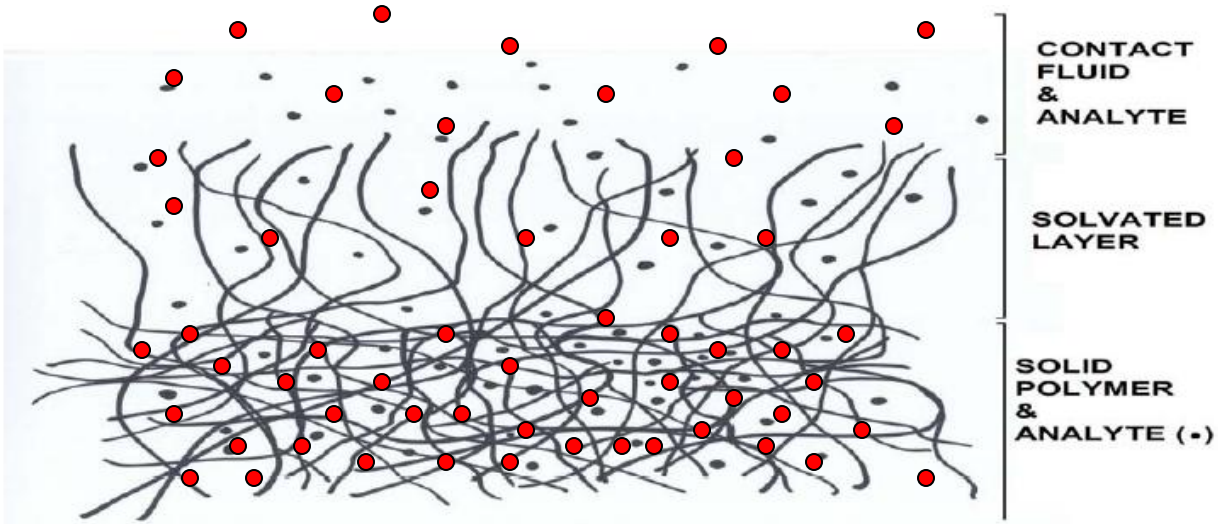
SOLVENT CAN "PLASTICIZE" or "SWELL" POLYMER:
SOLVATED LAYER



ENHANCED DIFFUSION OF LEACHABLES

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ACCELERATED LOSS

Thank you!