USING PREFIXES

Words which start with 'm' or 'p' take the prefix 'im-' (impatient, impossible)

But there are certain 'p' words whose opposite is prefixed with un- (unpolluted, unplugged)

Words which start with 'r' take 'ir-' (irresponsible, irregular)

Words which start with 'I' take 'il-' (illegitimate, illegal)

Use "non" - (non-smoker, non-alcoholic beverage, non-skid tires)

The "un" prefix is used to make descriptive words- (unjust, unethical, uneducated, unhappy)

Or to negate a verb- (unlock, unfold, unhook, undress)

A note of caution, though; while the above prefixes can only be used with the letters shown, the letters themselves are often used with other prefixes (unreliable, unlawful, unpatriotic)

mis- always has the sense of a mistake being made (misunderstand, misfire)

dis- has the sense of change or difference rather than absence/lack, e.g. "dissatisfied" means that you're not happy with the quality of something that you've got, whereas "unsatisfied" suggests a lack of something. (If you're dissatisfied with your restaurant meal you complain; if unsatisfied, you order more.)

With most other prefixes, it's not so much a question of rules as of learning their meanings: Pre- means before, post- after, and so on.